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Three types of potassium ion-selective electrodes were evaluated for suitability in monitoring or in-situ measurement applications. Each sensor was tested for the following parameters: accuracy, precision, temperature dependence, short and long-term stability, durability, sensitivity to variations in light intensity and flow conditions, response time as a function of temperature and potassium concentration, and variations between different manufacturers. The three potassium sensors (glass-membrane single electrode, glass-membrane combination electrode and liquid ion-exchange electrode) were evaluated at 10°C and 25°C in freshwater, synthetic seawater and natural seawater (35-, 20- and 5-ppt salinity). A description of the devices, the theory of their operation and a summary of the test results are included. Although all three electrodes performed well in freshwater, the results with the liquid ion-exchange electrode in seawater were significatly better than those with glass membranes. An accuracy of 5% in concentration could be achieved with some of the sensors when properly and frequently calibrated. The response times (95%) were unexpectedly long for all the sensors and were generally greater than 10 minutes. While none of the electrodes were affected by changes in light intensity, the two glass-membrane sensors were sensitive to external motion and flow variations.

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by

Gary K. Ward
National Ocean Survey
National Oceanic and Atmospheric Administration
Rockville, Maryland 20852

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FOREWORD

The Test and Evaluation Laboratory of the National Ocean Survey's Office of Marine Technology, National Oceanic and Atmospheric Administration, conducts work to:

- o test and evaluate new or state-of-the art sensors for use in the marine environment.
- o determine the error bounds on chemical sensors' performance to obtain data quality assurance information
- o determine suitability of new sensors for in situ or field use
- o evaluate new methods for the chemical analysis of seawater
- o develop standards and calibration equipment and procedures to maintain a quality assurance program for measurements in the marine environment.

New chemical sensors are under continual test and evaluation to assure that the most accurate results possible are obtained. If specific ion electrodes are to be used to measure chemical parameters in seawater, they must be evaluated directly in the medium of interest, i.e., seawater. This report investigates the basic characteristics of specific ion electrodes in a variety of water types to determine their suitability for in situ or monitoring applications.

E. M. Russin

Eugene M. Russin
Chief, Sensor Test Branch
Test and Evaluation Laboratory

ABSTRACT

Three different types of potassium ion-selective electrodes, manufactured by three different companies, were evaluated for suitability for application in monitoring or in situ chemical analysis systems. Each sensor was tested for the following parameters: accuracy, precision, temperature dependence, short- and long-term stability, durability, sensitivity to variations in light intensity and flow conditions, response time as a function of temperature and potassium concentration, and variations between different manufacturers. The three sensors (glass-membrane single electrode, glass-membrane combination electrode, and liquid ion-exchange electrode) were evaluated at 10°C and 25°C in freshwater, synthetic seawater (35-, 20-, and 5-ppt salinity), Atlantic Ocean water (35- and 20-ppt salinity), and Chesapeake Bay water (5-ppt salinity). A description of the devices, the theory of their operation, and a summary of the tests and results are included. Although all three electrodes performed well in freshwater, the results with the liquid ion-exchange electrode were significantly better in seawater than those with the two glass-membrane electrodes. An accuracy of 5% in concentration could be achieved with some of the sensors when properly and frequently calibrated. The response times (95%) were unexpectedly long for all the sensors and were generally greater than 10 minutes. While none of the electrodes were affected by changes in light intensity, the two glass-membrane sensors were sensitive to external motion and flow variations.

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LIST OF ABBREVIATIONS AND SYMBOLS

ABBREVIATIONS

ACS -- American Chemical Society
avg -- average
cm -- centimeter
elect - electrode
h -- hour
IAPSO - International Association for the Physical Sciences of the Oceans
IUPAC - International Union of Pure and Applied Chemistry
log -- logarithm
min. -- minimum
min -- minute
ml -- milliliter
mV -- millivolts
ppt -- parts per thousand

SYMBOLS

A -- activity
a_i -- ionic activity
Ag -- silver
AgCl -- silver chloride
Cl -- chloride ion
E -- electrode potential
E° -- electrode constant
F -- Faraday's constant
I -- ionic strength
°K -- degrees Kelvin
K^+ -- potassium ion
KCl -- potassium chloride
M -- molarity
Na^+ -- sodium ion
R -- universal gas constant
S -- electrode slope
T -- temperature
T_1 -- response time within 1 mV
T_{95} -- 95% response time
z -- ionic charge
γ -- activity coefficient
$\sim$ -- approximately

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SECTION 1

INTRODUCTION

The ideal analytical instrument in potentiometric chemical measurements would be an electrode which is sensitive only to a single substance among all the other constituents in the system. This requirement is met, to a certain extent, when membrane systems form the basis of ion-selective electrodes. These devices develop an electrical potential proportional to the logarithm of the "activity" of that ion in solution. The "activity" of an ion is proportional to the concentration of the ion. Generally, an electrode of this type is "selective" for one chemical parameter, i.e. although the membrane potential can be affected by more than one type of ionic species, the electrode selectively favors one specific ion on a response basis. Due to this selectivity, as well as for durability and compactness, potentiometric sensors are attractive devices for continuous water quality monitoring, either as in situ probes or as components in chemical analysis systems. They would eliminate the use of discrete samples and thereby provide an ideal method for obtaining truly representative measures of water parameters. The environment itself would become the sample, eliminating the sampling contamination and time lag which occurs between sampling and analysis and during which chemical and biological alterations take place.

Presently, ion selective electrodes are available for many chemical parameters and are used in marine chemistry research, effluent and pollution monitoring, mixing studies, and baseline surveys. Several commercial water quality systems offer capabilities for specific ion electrode measurements in freshwater, estuarine, and seawater environments.

In addition to the recent availability of specific ion electrodes for many chemical parameters, there are several other advantages to their use as analytical tools:

1. simple and relatively fast measurements
2. inexpensive and portable
3. capable of non-destructive analyses
4. adaptable to automatic measurands
5. capable of real-time measurements
6. continuous response for monitoring applications
7. small sample requirements
8. potential in situ appplication

Unfortunately, there are also some problems in electrode measurements. The major difficulty is that the electrodes respond to the activity of the ion, not the total concentration. The "activity" of an ion can be thought of as the "effective concentration" of the free ion in

solution, and is affected by temperature, pressure, ionic strength (a chemical parameter related to the number of other ions in the solution), and ionic interactions such as ion-pair formation or complexation. Even if the electrodes were truly specific, they would respond only to the free ion activity and, since many chemical species in natural waters are complexed with other ions or adsorbed on particulates, a large fraction may not be measured by these sensors. It is held by some scientists, however, that it is the concentration, or activity, of the free ion that is actually needed to evaluate the true effect of the species in the water column. This controversy is purely academic since at this time there is no method to accurately calculate individual ionic activities in solutions of mixed composition. Calibration problems occur, therefore, when the electrodes are used in complex solutions such as seawater.

A second disadvantage with specific ion electrodes is that they were not developed as highly accurate devices and are subject to a number of possible interferences (particularly in seawater) in addition to a certain amount of instability or drift. Most of these problems can be overcome with future development of selective membranes and frequent calibration with the appropriate standard solutions. There is a need for the development and evaluation of simple, rugged sensors for in situ measurements as opposed to jury-rigging the already complicated colorimetric or titrimetric analyses.

Recently, there has been a great deal of interest in ion-selective electrodes but very little work has been done on the performance and behavior of these devices in seawater or on their suitability as in situ sensors. The accuracy, precision, reliability, and durability of these electrodes must be known before they can be used for meaningful measurements.

The potassium ion-selective electrode can be used directly in seawater or freshwater without sample pretreatment and therefore lends itself to direct in situ applications. In this study, three potassium electrodes were evaluated:

1. Potassium Specific Ion Electrode #93-19 manufactured by Orion Research, Inc.

2. Potassium Electrode #4202-Q10 from Arthur H. Thomas Company

3. Combination Potassium/Ammonium Selectro-Mark Electrode #1018 from Markson Science, Inc.

SECTION 2

CONCLUSIONS

CALIBRATIONS

Freshwater

(1) None of the electrodes exhibited a pure Nernstian behavior with a Nernst theoretical slope, although the Thomas Potassium Electrode did exhibit the theoretical slope in one run in freshwater. Because of this erratic behavior, the calibration slope must be determined experimentally, and meters which assume the theoretical slope cannot be used for reliable data collection.

(2) Since none of the potassium electrode responses were linear with concentration, an experimental working curve of millivolts versus known concentration must be constructed. At least two calibration points should be used to closely bracket the potassium concentration in the unknown sample since the calibration non-linearity can become quite severe under certain conditions.

(3) All three electrodes had significant drift problems (Orion the least) and therefore require frequent calibration (at least twice daily). Because of the drift, the sensors cannot be used for continuous monitoring unless a method is provided for frequent, periodic recalibration.

(4) Whenever possible, the sample and standard should be measured at the same temperatures. If this is not possible, a temperature correction to the calibration curve can be generated. The Markson Potassium Electrode was relatively unaffected by temperature variations, particularly at high concentrations, and therefore its potential readout could easily be corrected for temperature changes.

(5) Potassium electrodes cannot be expected to give results with greater than 5% accuracy in freshwater or seawater.

(6) Electrodes from the same manufacturer have the same basic characteristics, but the electrode potentials for the potassium activity can vary significantly between sensors. This requires that each sensor be evaluated for its individual characteristics before being employed as a sensing device.

(7) Electrode stability increased after approximately 2 weeks of use for the Markson and Thomas electrodes. The Orion liquid ion-exchange electrode became remarkably stable after dropping to a low temperature (10°C) and returning to room temperature.

Seawater

(1) The glass membrane sensors (Thomas and Markson) did not perform as well in seawater as the liquid ion-exchange electrode (Orion). The latter was nearly linear in seawater at various salinities and in freshwater, while the glass sensors had very nonlinear responses in seawater. For all three sensors, however, frequent calibration in standard seawater solutions at the salinity of the sample is necessary. The Markson electrode was very sensitive to salinity variations and must be calibrated carefully. The Orion and Thomas potassium electrodes were relatively insensitive to salinity variations in seawater samples higher than 20-ppt salinity, and therefore could be calibrated in standard seawater solutions within the general salinity range of the sample.

(2) Background and matrix effects can be eliminated or reduced by either: (a) the standard addition method, or (b) duplication of the sample matrix in the standard calibration solutions. For in situ applications, the standard addition method is difficult and impractical. Reduction of the matrix problems was accomplished fairly well in this study with carefully prepared synthetic seawater standards for salinities 20 ppt or higher.

Response Times

(1) Electrode response was much slower than expected and was sometimes difficult to determine due to high drift rates. In general, the sensors do not reach 95% of the final value for a minimum of 10 minutes. A rapid response does occur in some cases but usually involves an initial over-response followed by a slow recovery to some final value.

(2) All the sensors responded faster to an increase in concentration than a decrease in concentration, indicating the possibility of a slight memory effect.

(3) For some electrodes (notably Orion), the time response curves were independent of potassium concentration. In these situations, a generalized response curve, over a range of potassium values, could be developed and the final value obtained by extrapolation of the first few minutes of sensor readings along that curve.

(4) Neither the response time nor the stability of the sensor is a function of whether an internal or external reference electrode is used.

(5) Response was much slower at low temperatures.

GENERAL CONCLUSIONS

(1) The electrode potentials were not affected by the height of the filling solution as long as they were kept above the level of the sample solutions to maintain a positive outward flow.

(2) The Orion Potassium module did not last as long as expected and failed after 3 months. (Module is under guarantee for 6 mo.)

(3) The glass electrodes were not as durable as the plastic Orion electrode. The body of the Markson sensor cracked in shipment, but was quickly replaced by the manufacturer. The Thomas potassium electrode developed an extreme sensitivity to motion of the connecting wire and was also replaced promptly by the manufacturer.

(4) The glass membrane electrodes were more sensitive to variations in flow around the sensor than the liquid ion-exchange sensor.

SECTION 3

RECOMMENDATIONS

RELIABLE DATA ACQUISITION

(1) Soak electrodes for at least 1 week in media similar to the samples, and subject them to low temperatures ($10^{o}C$) during this time to "break" them in.

(2) Perform a detailed calibration in standard solutions with the same background matrix as the sample and at the same temperature.

(3) Recalibrate the electrodes at two points near the sample concentration at least twice a day.

(4) Wait at least 15 minutes for the electrode response to stabilize.

(5) Before using the sensors, evaluate each one for general response characteristics, calibration linearity, daily drift, and temperature dependence. This would not take long and could be easily done in the lab before laboratory or field use.

FUTURE DEVELOPMENT

(1) Reinforce wire connections to the electrode.

(2) Reduce time response or make the response more reproducible.

(3) Stabilize electrode potential over a short time (1 d)

(4) Develop a combination electrode with refillable and removable reference electrodes, which could eliminate some interference problems by allowing variations in the filling solution and would also permit continued use of the sensor if the reference should fail.

SECTION 4

EXPERIMENTAL PROCEDURES

INSTRUMENT DESCRIPTION

Three different types of potassium sensors were evaluated in this study. (See Figure 1.) The Thomas Potassium Electrode #4202-Q10, manufactured by Arthur H. Thomas Company, employed a glass bulb membrane and required an external reference electrode. The Combination Potassium/Ammonium Selectro-Mark Electrode #1018, manufactured by Markson Science, Inc., was a combination electrode (requiring no external reference electrode) with a glass bulb membrane. The internal reference electrode was a sealed silver/silver chloride reference electrode and required no rejuvenation of the internal filling solution. The Orion Model 93-19 Potassium Specific Ion Electrode, manufactured by Orion Research, Inc., was a liquid ion-exchange electrode with a porous organophilic membrane which also required an external reference electrode. The Orion sensor consisted of an electrode body and a replaceable "pretested" sensing module which contained a gelled internal filling solution, a membrane saturated with liquid ion-exchanger, and a reservoir of liquid ion-exchanger. To activate the sensor, the module was simply screwed into the electrode body.

The external reference electrode was an Orion 90-01 Single Junction Reference Electrode constructed as a sleeve-type Ag/AgCl reference electrode designed for precision measurements in conjunction with specific ion electrodes. (See Appendix-Instrument Theory.) With this type of sensor, we were able to compare the glass-bulb membrane against the liquid ion-exchange electrode, and a combination electrode against a two-electrode system.

The electrode potential was read on an Orion Model 801A Digital pH/mV meter and a Corning Digital 112 Research pH meter. Both meters had a range of $\pm$1999.9 mV in 0.1 mV increments, with $\pm$0.1 mV repeatability. The high impedance input signals from the electrodes were amplified and fed into an analog-to-digital converter which produced a number of digital pulses proportional to the analog voltage input. These pulses were counted, and the digital information was decoded and used to determine the numbers displayed on the meter. The meters feature high input impedance, extremely low drift, and an output in absolute millivolts. The meter drift was determined by placing a shorting strap across the terminals. The drift of both meters was less than 0.2 mV in 6 months. Response time lag was found to be less than 5 seconds by rapidly switching from standby to millivolt measurement.

The sensing electrodes were secured in a container top which sealed onto a polypropylene sample container, and all sensors were submerged

TABLE 1. MANUFACTURERS' SPECIFICATIONS FOR POTASSIUM SENSORS

	Orion	Markson	Thomas
Concentration range	1 to 10^{-5}M	1 to 10^{-4}M	1 to 10^{-4}M
pH range	1 - 12	6 - 9	5 - 9
Temperature range (°C)	0 - 50	--	0 - 70
Elect. resistance (megohms)	0.1 - 0.3	--	--
Sample	aqueous only	aqueous	aqueous
Min. sample size	3 ml	--	--
Storage	dry (air)	dry	dry
Life	6 months	--	--
Electrode length[a]	13.5 (13.9)	(12.7)	13.4 (13.4)
Cable length	75 (84)	(74)	76 (80)
Electrode diameter	1.2 (1.5)	(1.6)	1.6 (1.6)
Soaking time (h)	0	1	24
Temperature effect[b]	2%	--	--
Reproducibility	±2%[c]	--	--
Response time	< 1 min (99%)[d]	--	--

[a]Values in parenthesis are actual dimensions.

[b]Temperature effect for a 1° change.

[c]With calibration every hour.

[d]For concentrations greater than 10^{-5}M.

approximately 4 cm into the sample solution. The submersion depth was kept constant throughout the tests, and the sample container was sealed to prevent evaporation. The sample container was submerged in a non-metallic constant temperature bath and rested on a Troemner submersible magnetic stirrer. A star-head Teflon magnetic stirrer agitated the solution inside the sample container. The non-metallic temperature bath was contructed to eliminate any possible stray electrical interferences which often occur in metal baths. The temperature was controlled to $\pm 0.01^{\circ}C$ with a Fisher Proportional Temperature Controller and a Neslab PBC-4 Bath Cooling Coil. A Hewlett-Packard quartz crystal thermometer monitored the temperature and was periodically calibrated against a platinum resistance thermometer and Mueller bridge. Sample solutions were suspended in the bath prior to each run to eliminate temperature effects on the electrode response.

The seawater samples were measured for salinity on a Guildline Model 8400 Laboratory Salinometer (Autosal) which has been evaluated and described in detail by the National Oceanographic Instrumentation Center (NOAA Technical Memorandum NOS 18, July 1976). The seawater samples were analyzed for potassium on a Perkin-Elmer Model 503 Atomic Absorption Spectrophotometer. The calibration curves and fits were determined by a least-squares regression program on a Hewlett-Packard "9825" Calculator.

The freshwater standard solutions were prepared with Fisher Certified ACS Reagent grade potassium chloride which was oven-dryed for several hours and cooled in a desiccator. The standard solutions were prepared by weight with Millipore ion-exchanged (18 megohm) water and dried potassium chloride without further purification. Following the formula of Kester (1967), the synthetic seawater was prepared from Fisher Certified ACS reagents: sodium chloride, sodium sulfate, potassium chloride, sodium bicarbonate, potassium bromide, boric acid, sodium fluoride, magnesium chloride (hydrated), calcium chloride, and strontium chloride (hydrated). The synthetic seawater at 20- and 5-ppt salinity were prepared by weight-diluting the artificial 35-ppt seawater with pure water.

The "unknown" natural water samples were IAPSO standard seawater (P66 27/7, 1974-Cl ppt. = 19.3675), Atlantic Ocean water (32.176-ppt salinity from a station at 38° 40.3'N and 74° 20.0'W), and Chesapeake Bay water (4.159-ppt salinity). The IAPSO standard seawater was weight-diluted with pure water to obtain 20- and 5-ppt salinity seawater. The Atlantic Ocean water was prepared in a similar manner to 20-ppt salinity. The diluted IAPSO seawater samples provided a test for salinity effects with no compositional changes. The Chesapeake Bay water provided samples with polluted estuarine waters.

Since the purpose of this study was to evaluate the potential use of potassium sensors directly in natural water environments, no reagents were added to the samples to remove ionic strength effects or ionic interferences. In pure water, theoretical calibration curves were

determined using activities of potassium ions calculated from the activity coefficient data of Robinson and Stokes (1965) to determine if the sensors truly exhibited Nernstian behavior. In seawater samples, however, a working curve was prepared as a function of salinity, since the theoretical Nernst slope is valid only in pure water.

TEST PROCEDURES AND RATIONALE

Each electrode was evaluated in freshwater at 10°C and 25°C, and in five different water types at 25°C: pure water, synthetic seawater, IAPSO standard seawater, Atlantic Ocean Water, and Chesapeake Bay water. The pure water runs were performed to observe basic electrode characteristics with no chemical interferences and only slight ionic strength effects. The synthetic seawater runs were used to study the electrodes in a known-composition solution which simulated natural seawater and its possible matrix effects. The IAPSO standard seawater runs were made at 35-, 20-, and 5-ppt salinity to determine the salinity effect without possible compositional changes. Clean Atlantic Ocean water was used to study differences between IAPSO seawater (treated Atlantic water) and natural ocean water (for possible organic effects); the Chesapeake Bay water provided samples with an estuarine matrix and possible pollutant interferences.

Calibration curves in pure water were obtained for each sensor by measuring the potassium activity in seven standard solutions ranging from 1×10^{-3} M to 1.0 M KCl. Two calibration runs were made at 25°C, the first in decreasing concentration steps, the second in increasing concentration steps. With this procedure, we could determine the effect of increasing and decreasing concentrations on calibration curves and response time in addition to the short-term drift, or reproducibility, between the two runs. The electrodes were then calibrated at 10°C in the same standard solutions and again at 25°C. From these runs, we could determine the effect of increasing and decreasing temperature on calibration curves and response times, long-term drift at 25°C (from the first two runs), and durability from temperature changes. During each calibration the sensors were tested for: (1) short-term drift (3 h); (2) sensitivity to flow variations; (3) sensitivity to changes in light intensity; (4) sensitivity to motion of the electrode and the connecting wire; (5) variations in electrode potential due to changes in filling solution heights; and (6) response time.

Calibration curves in synthetic seawater solutions were obtained for each electrode by measuring the potassium activity in four standard seawater solutions, which were prepared by adding known amounts of KCl salt to the synthetic seawater mixture. Immediately after calibration, potassium activity readings were obtained in the two natural water samples. This procedure was completed at three salinities: 35, 20, and 5 ppt. The natural water samples were: (1) IAPSO standard seawater and Atlantic Ocean water at 35-ppt salinity, (2) diluted IAPSO standard seawater and diluted Atlantic Ocean water at 20-ppt salinity, and (3) Chesapeake Bay water and diluted IAPSO standard seawater at 5-ppt salinity. The concentrations of K^+ in the natural water samples were also measured by atomic absorption spectrophotometry. From the electrode seawater runs, we determined the effect of salinity on the electrode potentials and response times, stability in various water types,

sensitivity to changes in light, organic and/or other interferences, and suitability for possible in situ monitoring in freshwater, estuarine, and seawater environments.

SECTION 5

RESULTS

CALIBRATIONS

Three calibrations were run at 25°C, one was run at 10°C, and one was run in 35-, 20-, and 5-ppt salinity seawater. Each electrode was soaked in a 0.01 M KCl solution for 1 week prior to the tests. All concentrations are given in molarity, defined as moles of potassium per liter of solution.

The electrode potentials in each solution varied a great deal between the different sensors. In 0.01 M KCl at 25°C, for example, the sensors had potentials of -99.5, -0.3, and -131.5 mV for the Thomas, Markson, and Orion electrodes, respectively. Electrode potential also varied between electrodes from the same manufacturer. For example, in 0.01 M K^+ (the potassium concentration in seawater), two sensors from the Thomas Company had values of -99.5 and -19.8 mV, and two Orion sensors had values of -131.5 and -74.0 mV in the same standard solutions. Obviously, the absolute value of the potential in millivolts is very dependent upon the characteristics of each individual sensing electrode and the reference electrode used for measurements, and can only be determined empirically by calibration in standard solutions.

In pure water, the electrode potential was first plotted as a function of concentration and activity. The activities of the potassium ion in freshwater were determined from the mean activity coefficient ($\gamma\pm$) data for KCl from Robinson and Stokes at 25°C. The McInnes convention was employed to separate $\gamma\pm$ into ionic components [i.e., $\gamma_+(K^+) = \gamma - (Cl^-)$]. The logarithm of the potassium activity was fitted to the electrode potential with the equation

$$E = E^o + S \log A \qquad (1)$$

where S should be the theoretical Nernst slope (59.16 at 25°C), E^o is the intercept, and A is the activity of potassium ions. The coefficients, E^o and S, are given for all the sensors at 25°C in Table 2. The precision is included as the standard deviation.

The logarithm of the potassium concentration (M) was also fitted to the electrode response. Since the curves were not always linear, the data were fitted to the equation

$$E(mV) = A + B \log M + C (\log M)^2 \qquad (2)$$

where A is the intercept, B is the empirical slope, and C is the non-linearity, or deviation, from the linear slope. Since the activity of the potassium ions was not equal to the concentration, all the calibration curves were non-linear; the coefficients for Equation (2) are given in Table 3 for the freshwater and seawater calibration runs.

TABLE 2. COEFFICIENTS FOR THEORETICAL NERNST EQUATION ($E = E^{o} + S \log A$) at 25°C FOR POTASSIUM SENSORS

Calibration run		E^{o}	S	Standard deviation
			Thomas	
FW	#1	34.13	65.32	3.4
	#2	31.40	59.95	3.5
	#3	110.88	65.15	0.3
			Markson	
FW	#1	93.48	49.84	3.8
	#2	84.26	46.56	2.3
	#3	84.38	43.33	1.3
			Orion	
FW	#1	1.95	66.97	6.1
	#2	-68.97	54.95	6.5
	#3	60.34	66.00	2.0

TABLE 3. EMPIRICAL CALIBRATION CURVE COEFFICIENTS FOR THE POTASSIUM ELECTRODES

Calibration		A	B	C	Standard deviation
			Thomas		
Freshwater					
(25°C)	#1	24.45	60.81	-0.44	4.5
	#2	16.51	48.22	-2.40	3.1
	#3[a]	96.04	56.98	-0.80	0.3
(10°C)	#1	48.30	34.74	-5.12	1.2
Seawater					
35 ppt		115.32	71.50	15.94	0.1
20 ppt		122.84	70.21	12.58	0.2
5 ppt		123.86	85.38	12.88	---
			Markson		
Freshwater					
(25°C)	#1	79.28	35.41	-3.60	2.9
	#2	72.47	36.88	-2.06	2.9
	#3	73.84	36.44	-1.09	1.0
(10°C)	#1	74.11	36.78	-0.43	1.0
Seawater					
35 ppt		66.27	-7.89	-7.66	0.1
20 ppt		57.49	7.87	0.74	0.4
5 ppt		58.82	35.76	6.56	0.4
			Orion		
Freshwater					
(25°C)	#1	-16.56	54.47	1.32	5.6
	#2	-19.17	42.17	-6.70	2.7
	#3	42.07	50.77	-3.46	1.1
(10°C)	#1	42.38	40.46	-4.69	1.2
Seawater					
35 ppt		45.99	39.91	-4.99	0.4
20 ppt		44.72	41.80	-3.06	0.5
5 ppt		53.68	59.53	1.31	0.1

[a]New sensor.

Freshwater - 25°C

Thomas Potassium Electrode--

The Thomas sensor was very unstable at high concentrations in Run #1, although it had been soaking in a KCl solution for 7 days prior to the evaluation (6 days of soaking was recommended by the manufacturer as the time required for optimal stability). The electrode response is plotted as a function of potassium activity in Figure 2. The slopes of the calibration curves (electrode response as a function of the log of the activity) for the three freshwater runs were 65.3, 60.0, and 65.2 mV, respectively, compared to the theoretical value of 59.2 mV calculated from the Nernst equation (Equation 3). The third calibration run was completed with a new Thomas electrode (the original sensor had ceased to function) and behaved very much like the first electrode. Both sensors had a linear response to the logarithm of the activity, indicating that the electrodes do respond in a Nernstian manner.

The calibration curves in freshwater are shown in Figure 3 as a function of the log of concentration. Calibrations 1 and 2 were done with the first Thomas electrode and were 6 days apart. The coefficients for the calibration curves changed considerably from Run #1 and Run #2: The intercept (term A in Equation 4) decreased 33% (8 mV); the slope (B term) decreased 21% (12.6 mV); and the non-linearity (term C in Equation 4) increased from -0.4 to -2.4. The large decrease in the slope reflects a reduction in the sensitivity with usage. The significant drift that occurred in 6 days emphasized the point that the sensor must be calibrated at least once a day to obtain results within 10%. It should also be noted that although the slope of the new electrode in Run #3 was only 6% different from that of the original in Run #1, there was a large difference in electrode potential (70 mV), indicating that large variations are possible in potentials of sensors from the same company.

Markson Potassium Electrode--

The Markson sensor was also unstable during the initial tests, but settled down after 1 week in operation. The manufacturer's instructions had recommended only 1 hour of soaking before use. Although the electrode responses were a linear function of the log of the potassium activity (see Run #1 in Figure 4), the experimental slopes of 49.8, 46.6, and 43.3 mV for Runs #1, #2, and #3, respectively, did not compare favorably with the theoretical Nernst value of 59.2 mV; this indicates that the sensor was less sensitive to changes in potassium activity than expected from theory.

The electrode response as a function of concentration gave encouraging results, however, as all three calibration curves were very similar (Figure 5). The slope term changed only 4% over a period of several weeks (only 1% between Runs #2 and #3), and the intercept

increased only 2%. The non-linearity decreased slightly with each run until the electrode response was nearly linear by Run #3. In freshwater the Markson electrode showed very little drift after 1 week of operation, resulting in less frequent calibration requirements, but appeared to be less sensitive than the others to changes in potassium ion concentrations.

Orion Potassium Electrodes--

The Orion sensor also had stability problems in Run #1, particularly at low concentrations. However, the electrode became remarkably stable after the 10°C calibration, which could be due to either some stabilizing effect of the temperature drop or merely increased stability from usage. At 25°C, the electrode response was a linear function of the potassium activity (Figure 6) and behaved as a Nernstian device, although the standard deviation was somewhat larger for the Orion than for the other sensors. The experimental slopes for Runs #1, #2, and #3 were 66.9, 55.0, and 66.0 mV, respectively, and compared favorably to the theoretical slope of 59.2 mV.

From the calibration curves as a function of concentration, shown in Figure 7, it is apparent that the electrode potential did not drift once it had stabilized at concentrations $\geq$0.01 M K^+ (the concentration of potassium in seawater) for the first two runs. At lower concentrations, however, the Orion sensor failed to stabilize to less than $\pm$1 mV in Runs #1 and #2, and therefore was very difficult to calibrate below 0.01 M K^+. After the 10°C run, the subsequent 25°C calibration had a slope within 7% of Run #1, although the entire curve was offset by 58 mV at the intercept.

In general, the slope of the Orion electrodes was linear and changed relatively little over a period of weeks in freshwater solutions; therefore, a daily recalibration at only one concentration is sufficient (for an accuracy of 10%) to determine the offset from the complete calibration curve derived weekly. For greater accuracy (5%) at least two recalibrations per day, with at least three standard solutions are required.

Freshwater - 10°C

Theoretically, the slope of a device exhibiting Nernstian behavior should decrease by 3 mV/decade for the temperature drop from 25°C to 10°C. Two of the electrodes under evaluation were more than twice as sensitive to the temperature change as predicted by theory.

Thomas Potassium Electrode--

The calibration slope decreased by 6.5 mV/decade for the 15-degree temperature drop. (See Figure 8.) In addition to this, however, there was a large offset (46.2 mV at 0.05M) in electrode potential at 10°C and a

marked increase in non-linearity, indicating a sensitivity of Thomas potassium sensors to temperature fluctuations.

Markson Potassium Electrode--

The slope of the Markson potassium electrode changed only 2.6 mV/decade at 10°C (Figure 9), and the temperature effect on the intercept was only 0.3 mV. Other than the predictable slope change, the electrode appears to be relatively insensitive to temperature variations, particularly at high concentrations.

Orion Potassium Electrode--

The slope of the Orion potassium electrode decreased slightly more at 10°C than the Thomas sensor (7.5 mV decade, see Figure 10), but was similar to the Markson electrode in that the intercept changed only 0.3 mV for the temperature increase from 10°C to 25°C. Although the non-linearity was greater at 10°C, the electrode stability was significantly improved at 10°C. While the intercept (E^o in Equation 1) changed considerably (58mV) from 25°C down to 10°C, it did not change with the increase in temperature back up to 25°C.

In general, the slopes of the electrodes response decreased by 2 to 7 mV/decade for the 15-degree drop in temperature from 25°C to 10°C. While the intercept (in Equation 2) for the Thomas sensor changed significantly, the temperature variations had little effect on the intercept for the Orion and Markson sensors (0.3 mV). The results indicate that the most reliable data can be obtained by measuring samples at the same temperature ($\pm$0.5°C) as the calibration solutions. Since the intercept (E^o) for the Markson and Orion electrodes was not temperature dependent, sensor readings may be corrected for temperature fluctuations with only an adjustment of the slope term.

Seawater - 25°C

Thomas Potassium Electrode--

The seawater calibration curves for the Thomas sensor at 25°C are shown in Figure 11 as a function of salinity and potassium concentration. The non-linearity decreases with salinity until, at low salinity, a nearly linear relationship is observed. The large salinity effects emphasize that the electrodes must be calibrated in standard solutions with a background matrix similar to that of the sample. If the freshwater calibration were used for the seawater samples, the errors in potassium concentration would have been 210%, 203%, and 37% in 35-, 20-, and 5-ppt salinity IAPSO seawater, respectively. It is important to note, however, that the differences in electrode potential between the 20- and 35-ppt standards were not large (8%); therefore, a calibration of the electrode with standard solutions near 35-ppt salinity could be used for most ocean samples (30-37 ppt) without introducing significantly

large errors, since the high salinity appears to swamp out the ionic strength effects. Below 20 ppt, however, small variations in salinity can cause large errors unless the standard solutions are prepared close to the salinity of the unknown sample. Due to the increased non-linearity of the calibrations in seawater, the sensor should be calibrated with standard solutions close to and bracketing the concentration of potassium in the samples.

Markson Potassium Electrode--

The Markson sensor did not perform well in seawater solutions. It is apparent from Figure 12 that the sensor is severely affected by fluctuations of the background salinity. The non-linearity changed from -7.7 at 35-ppt salinity to +6.6 at 5-ppt salinity and resulted in some unusual calibration curves. The errors resulting from using the freshwater calibration curves at 0.01 M (K^+) were 210%, 183%, and 66% at 35-, 20-, and 5-ppt salinity, respectively. The data clearly show that the Markson sensor must be calibrated not only in standard solutions with the same background salinity, but also very near the potassium concentration in the sample to eliminate errors from the non-linearity of the curves.

Orion Potassium Electrode--

Figure 13 shows that not only was the Orion sensor relatively insensitive to large changes in salinity, but also the electrode response was very nearly linear at all salinities. The effect of salinity (5 to 35 ppt) was very small (only 1.5% error at 0.05 M K^+) and, therefore, standard solutions near 35-ppt salinity could be used for a wide range of concentrations and salinities in oceanographic or estuarine applications. It is still necessary, however, to calibrate the sensor in a seawater matrix, since errors resulting from using only the freshwater calibration would have been 144%, 91%, and 56% in 35-, 20-, and 5-ppt salinity, respectively.

In general, the glass bulb membrane sensors were severely affected by salinity changes and must be carefully calibrated in seawater solutions near the salinity of the samples. Based on the calibration data, the liquid ion-exchange sensor appears to be suitable for oceanographic use after calibration with seawater solutions at salinities within $\pm$ 5 ppt of the samples.

RESPONSE TIMES

The response times of the potassium electrodes are summarized in Table 4 in the following forms: internal 95% response time, T_{95} (I); external 95% response time, T_{95} (E); and the IUPAC-recommended response time, T_1. The first two forms are the 95% response times, which are defined as the time required for the system output to attain 95% of the asymptotic value when subjected to a step input, where T_{95} (I) differs from T_{95} (E) by the type of step change. The 95% response is equal to three "time constants" ($1-e^{-1}$) of a pure exponential response. The third response time, T_1, is the time required for the sensor to reach a value within $\pm$1.0 mV (3% in concentration) of the final electrode potential. The electrode output was monitored continously for 3 hours in each test solution, initiating from the moment the sensor was immersed. The T_{95} (internal), or T_{95} (I), is the time required for the electrode response to reach 95% of the change between the initial and final electrode potentials in the same standard solution. The T_{95} (external), or T_{95} (E), is the time required for the sensor output to reach 95% of the total change between the final potential in two consecutive test solutions at two different concentrations. The T_1 response time is considered to be the most useful parameter for evaluating the electrode equilibration time, since it is independent of the magnitude of the concentration step-change. All three methods of expressing the response time, however, are presently in use by various investigators.

The responses of each potassium sensor in freshwater and seawater have been plotted as "delta mV" versus time (minutes) at 10°C and 25°C. The "delta mV" term is the difference between the initial electrode potential obtained immediately after immersion in the solution and the potential output at time, T. In this manner, the electrode response at various concentrations (the Bottle numbers in the figures correspond to various levels of potassium concentration) could be easily depicted on one graph.

The calibration #1 at 25°C was performed by starting with the highest concentration standard, and proceeding in decreasing concentration steps to the lowest concentration standard. Freshwater Runs #2 and #3 at 25°C and the 10°C calibration were completed in reverse order, with progressively increasing concentration steps. The molarity of the standards correspond to the bottle numbers in the response curve plots as follows: 0.5 M in #2, 0.1 M in #3, 0.05 M in #4, 0.01 M in #5, and 0.005 M in #6.

Thomas Potassium Electrode--

The electrode response is shown as a function of time and potassium concentration in Figure 14 for freshwater solutions at 25°C. The response in Run #1 at high concentrations (>0.01 M) is characterized by a rapid response, a negative overshoot, and then a recovery to the final stable value. The recovery from the overshoot was usually very slow, and

TABLE 4. RESPONSE TIME (MINUTES) OF POTASSIUM ELECTRODES

	Thomas	Markson	Orion
Freshwater			
25°C, #1	51[a](79)[b],56[c]	30(43),32	57(82),56
#2	13(45),24	11(21),12	38(76),54
#3	28(52),28	9(29),19	1(29),6
10°C #1	32(66),24	21(32),22	57(75),50
Seawater			
5 ppt	25(30)	55(49),22	14(54),6
20 ppt	41(29)	56(41),21	1(11),1
35 ppt	20(19)	42(55),33	3(20),7

[a] T_{95} with initial potential equal to the electrode potential in the previous standard solution, $T_{95}(E)$.

[b] T_{95} (in parentheses) with initial potential at 0.3 minutes in the same solution, $T_{95}(I)$.

[c] Time required for electrode response to reach $\pm$1mV of the final value T_1 (recommended by IUPAC).

the response did not level off for more than 90 minutes. In the low concentration samples, the overshoot disappeared, and a "normal" response curve was observed. The electrode response in Run #2 was very similar to those at low concentrations in Run #1. Although the response curves in freshwater Run #3 (Figure 15) were obtained with a new Thomas electrode, it also exhibited the overshoot characteristic of the original electrode. This second sensor had a long positive overshoot at high concentrations, which decreased with decreasing concentration and eventually became negative, similar to that observed at low concentrations in Run #1. It should also be noted that, after the initial response period (60 min), the sensor drifted constantly $\sim$0.2 mV every 15 minutes.

At low temperatures (10°C), the overshoot observed in the 25°C runs became much larger and longer (see Figure 16), resulting in longer response times. At both temperatures, the potential in the low concentration samples was less stable than in high concentrations.

The sensor response in 35- and 20-ppt salinity synthetic seawater was characterized by a rapid response, followed by a general positive drift of $\sim$0.4 mv/15 min (see Figure 17) without the overshoot found in the freshwater samples. In 5-ppt salinity seawater, however, a long (30 min) overshoot was observed prior to the resumption of the positive drift found at the higher salinities (Figure 18). In IAPSO standard seawater, Atlantic Ocean water, and Chesapeake Bay water, the response was the same as in synthetic seawater at equal salinities, except that the drift was slightly greater. The similar responses in synthetic seawater and natural seawater indicate a general insensitivity of the sensor to dissolved organic components in natural seawater and possible pollutant interferences in Chesapeake Bay water; therefore, these electrodes could be used in natural waters after proper calibration with synthetic seawater (with respect to the response time). The similarity of the curves in seawater at high salinities would allow the characterization of a general response curve, then the calculation of a final value by extrapolation along that curve after a few minutes of initial readings. This would not be possible in freshwater, however, since the shape of the curves changed drastically with variations in concentration (Figures 14 and 15).

Markson Potassium Electrodes--

The response curves from the Markson sensor, given in Figure 19 for Run #1 in freshwater, were characterized by a rapid response, a positive overshoot, and finally a return to a stable reading (<0.1 mV/30 min). The time required for the sensor to recover from the overshoot, however, increased as the concentration decreased. The response in Run #2 was the same as in Run #1 except that the overshoot disappeared at high concentrations. The sensor stability, in contrast to the Thomas electrode, was not affected by concentration. The electrode response in freshwater for Run #3 (Figure 20) was similar to Run #1 except that the overshoot was not as pronounced and became negative at high

concentrations.

The low temperature calibration (10°C) was characterized by the same positive overshoot observed at 25°C that increased with decreasing concentration (Figure 21). The recovery from the overshoot, however, was much slower than that in the 25°C calibration.

The electrode time responses in synthetic seawater solutions (Figures 22 and 23) were remarkably independent of salinity, but varied considerably with changes in potassium activity. The electrode potentials were much less stable in the seawater runs and drifted in the negative direction by 0.2-0.9 mV every 15 minutes. The response in the high-and medium-salinity Atlantic Ocean water and standard seawater were similar to those in the synthetic seawaters at equal salinities except that the sensors were more stable, exhibiting drifts of only 0.2 mV/15 minutes or less. In the polluted low-salinity Chesapeake Bay water, however, the electrode rarely stabilized and, after 1 hour, continued to drift at a rate of 0.4 mV every 15 minutes.

In general, the response times were much slower in both synthetic and natural seawater, and the drift problems were much more severe. In unclean waters, the glass sensing membrane appears to be significantly affected, resulting in longer response times and an increase in drift. Since the response curves changed with potassium concentrations, it is not possible to prepare a general response curve in freshwater or seawater.

Orion Potassium Electrode--

The response curves of the Orion electrode in Run #1 of the freshwater calibrations at 25°C turned out to be rather unusual (see Figure 4). At the high and low concentrations, the overshoot characteristic for the other potassium electrodes was absent. In the middle concentration range, however, a negative overshoot was observed, and the electrode was generally unstable at high and low concentrations. In Run #2, similar behavior was found. After more than 2 hours, the electrode potential was still unstable ($\pm$.4 mV/15 minutes). Fortunately, Run #3 was completed after the 10°C runs and was found to be remarkably stable compared to the first two runs, with final values that varied less than 0.1 mV/15 minutes. (See Figure 24.) Although an overresponse was still found at concentrations >0.01M, the response curves were almost identical regardless of potassium concentrations. The temperature drop to 10°C between Runs #2 and #3 seems to have stabilized the sensor. (See Figure 26.)

The Orion electrode also behaved well in the synthetic seawater samples. The ΔmV curves in 35 and 20 ppt for all K^+ concentrations were nearly identical (<0.3 and 0.9 difference in ΔmV at 35 and 20 ppt respectively) and are shown in Figure 27 as a function of potassium concentration at 35-ppt and 20-ppt salinity. After approximately 20

minutes, there was a small negative drift of ~0.1 mV/15 minutes. Although the characteristic overshoot was not observed at 35 ppt, a slight overshoot was found at low concentrations in 20-ppt salinity seawater, which increased as the potassium concentration decreased. At 5-ppt salinity, the response curves were quite different from those at the higher salinities, but did not change significantly with variations in potassium concentration. (See Figure 28.) At this low salinity, all time response curves exhibited a negative over-response, characteristic of many electrodes in freshwater, which also increased with decreasing concentration.

The electrode time response was almost identical in Atlantic Ocean water and IAPSO standard seawater at equal salinities. However, unlike the synthetic seawater samples, the sensors responded very rapidly (<20 sec) in 35- and 20-ppt salinity samples then remained very stable for a short period (~10 min before the electrode potential began to drift 0.3 mV every 15 minutes. (See Figure 29.) The response in 5-ppt natural seawater (IAPSO standard seawater and Chesapeake Bay water) was very similar to that in the 5-ppt salinity synthetic seawater samples and therefore had the characteristic negative overshoot and recovery, followed by a positive drift. The large drift (0.6 mV/15 min), found in Chesapeake Bay water, was significantly greater than that in IAPSO seawater (0.4 mV/15 min) and indicates a susceptibility of the sensor to interferences in polluted waters.

In general, once the Orion sensor was stabilized at 10°C, the electrode response in freshwater and saltwater was almost independent of variations in potassium concentration and would permit the development of a general response curve from which final values could be extrapolated. In seawater, the sensor is also unaffected by salinity changes in solutions over 20 ppt and could be calibrated in solutions approximately equal in salinity to the unknown samples.

DRIFT

The drift of the electrode potential was monitored over three different time spans. The short-term stability was determined from the change in response from T_{100} for a period of 2 hours. The drift over 1 day was determined from the reading taken 3 hours after electrode immersion until the reading of the following day. The drift over 1 week was determined from the difference between the three calibration runs which were completed 1 week apart in the same standard solutions. Due to the large variations in absolute values for electrode potentials, longer drift tests were deemed unnecessary.

The hourly, daily, and weekly drifts are given in Table 5 for each sensor in freshwater. Since the electrode potentials rarely stabilized completely in the seawater solutions, the drift after 1 hour of readings is given in Table 6 for results in natural and synthetic seawater as a function of salinity. Also included in Table 6 is the average value for drift in freshwater at 10°C and 25°C. In general, the greatest drift in potential occurred at low concentrations during the first 5 hours, after which the sensors stabilized to 0.1 - 0.2 mV per hour.

The Thomas electrode had the worst short-term drift over the period of 1 day (16% error) in freshwater and was particularly bad in high-salinity (20 and 35 ppt) natural waters. The sensor had less drift in low salinity (5 ppt) seawater and freshwater. The Markson potassium electrode settled down with use (See Table 5), but exhibited excessive drift in IAPSO standard seawater at 35- and 20-ppt salinity. The drift in the potential of the Orion potassium electrode dropped significantly after the 10°C calibration but gradually increased with continued use in seawater solutions. (See Table 6.) There was also slightly less drift for the Orion electrode in synthetic seawater, relative to the natural seawater. The Orion electrode drift, however, was remarkably constant and predictable at all salinities (See Figure 27) and therefore could be treated as a drifting baseline.

ENVIRONMENTAL EFFECTS

The sensitivity of each sensor to light and flow variations and to external motion of the electrode body and wire is given in Table 7. Although none of the sensors were sensitive to changes in light intensity, the Markson electrode and the first Thomas electrode were very dependent on flow around the sensor. The Orion was fairly stable under all environmental conditions.

TABLE 5. DRIFT (mV)[a] OF ELECTRODE POTENTIAL IN FRESHWATER

Time range	Thomas	Markson	Orion
T_{100}[b] to 2 hours			
Run #1	0.6	0.8	0.8
Run #2	0.7	0.3	0.7
Run #3	0.4	0.2	0.2
1 day[c]	4.3	3.4	2.6
1 week (average)	5.7	7.3	4.4
1 week[c]	6.0	11.7	18.6

[a]Drift of 2 mV corresponds to an error of 7.5% in concentration.

[b]T_{100} is the time at which sensor stabilized after initial response.

[c]Worst case values.

TABLE 6. ELECTRODE DRIFT IN SEAWATER[a]

Water type	Thomas	Markson	Orion
35 ppt (1) synthetic	0.3	0.5	0.2
(2) IAPSO	0.4	1.2	0.3
(3) Atlantic Ocean	0.6	0.1	0.2
20 ppt (1) synthetic	0.4	0.3	0.1
(2) IAPSO	0.0	0.8	0.3
(3) Atlantic Ocean	0.6	0.1	1.3
5 ppt (1) synthetic	0.2	0.4	0.3
(2) IAPSO	0.3	0.1	0.4
(3) Chesapeake Bay	0.1	0.4	0.5
0 ppt (1) 25°C[b]	0.4	0.1	0.4
(2) 10°C	0.3	0.1	0.5

[a]Drift in terms of change in mV every 15 minutes after 45 minutes of readings (0.2 mV = 0.8%).

[b]Average value for all three runs.

TABLE 7. ENVIRONMENTAL EFFECTS[a]

Parameter	Thomas[b]	Markson	Orion
Light variation	0	0	0
Flow variation	9.9,0.1	6.0	0.2
External motion	±14, ±0.4	±4.5	±0.2

[a]Change in electrode potential (mV).

[b]Two values are given for Thomas. The first value corresponds to the first Thomas sensor in Runs #1 and 2. The second value is for the second Thomas electrode after the first sensor failed at 10°C.

ACCURACY

The accuracy of each sensor in natural waters was determined by comparing the value obtained from the electrode, after calibration in seawater, to the value obtained by atomic absorption analysis. The errors are given in Table 8 as percent deviation of the electrode values from the true concentration of potassium in each of the natural water samples. The electrode concentration values were obtained from the electrode potential after 1 hour of response. The electrodes were calibrated with four standard seawater solutions, followed immediately by the determination of the unknown concentrations the same day. The large errors from the glass-membrane sensors may be due to the drift of the electrode potential in seawater. (See Table 6.)

TABLE 8. ACCURACY[a] OF POTASSIUM ELECTRODES IN SEAWATER

Salinity (ppt)		Thomas	Markson	Orion
35	IAPSO	25.6	27.0	1.0
	Station A	36.8	35.1	2.5
20	IAPSO	43.6	44.9	3.0
	Station A	6.7	5.7	0.2
5	IAPSO	1.3	99.7[b]	28.0
	Chesapeake Bay	57.7	47.9	11.0

[a]Accuracy is expressed as percent error, % error = $100 \frac{(\text{observed-true})}{(\text{true})}$.

[b]Extreme drift problems.

REFERENCES

Boyd, J.E. 1976. Performance Evaluation of Guildline Model 8400 Laboratory Salinometer. NOAA Technical Memorandum NOS 18 (PB 259696), National Ocean Survey, NOAA, Rockville, Md. 20 pp.

Kester, D.R. 1967. Preparation of Artificial Seawater. Limnol. Oceanog. 12, 176.

Robinson, R.A. and R.H. Stokes. 1965. Electrolyte Solutions. Butterworths, London. 571 pp.

BIBLIOGRAPHY

Bates, R.G. 1973. Determination of pH - Theory and Practice. John Wiley and Sons, New York. 479 pp.

Durst, R. 1969. Ion-selective electrodes. National Bureau of Standards Publication 314, Washington, D.C. 452 pp.

Koryta, J. 1975. Ion-selective electrodes. Cambridge University Press, Cambridge. 207 pp.

Riley, J.P.,and G. Skirrow. 1975. Chemical Oceanography (Vol. 4), Academic Press, New York. 363 pp.

APPENDIX - INSTRUMENT THEORY

Ion-selective electrodes generally have a sensing membrane which allows only the ion of interest (potassium in this study) to pass from the sample solution at the outer membrane surface to an internal solution in contact with the inner membrane surface. The internal solution contains a fixed activity of the ion to which the membrane is permeable. When the electrode is placed in a sample solution, there is a momentary flux of ions across the membrane in the direction of the solution containing the lower activity of the mobile ion. Since the ions carry a charge, an electrical potential is set up which opposes further ion migration. Eventually, an equilibrium is established in which the potential across the membrane is exactly that required to prevent further net movement of ions.

Changes in the membrane potential can be measured by making electrical contact to the inner solution with a suitable reference electrode. At the same time, the sample solution is in electrical contact with a second reference electrode via a salt bridge. In some electrodes, this second reference electrode is contained inside the body of the ion-selective sensor which is therefore referred to as a "combination electrode." A high input impedance voltmeter connected across the two electrode leads will indicate a potential given by the Nernst equation

$$E = E^\circ + 2.3 \frac{RT}{zF} \log A \qquad (3)$$

where E is the potential in millivolts developed by the system. The term E° is a constant which depends on the particular choice of reference electrode used, the choice of ion-activity in the inner solution, and the small potential due to the liquid-liquid junction at the salt bridge connection. The term RT/zF is the Nernst factor where R is the universal gas constant, T is the temperature (°K), and F is Faraday's constant. The value of the Nernst factor at 25°C is 59.16 mv per decade. The term A is the activity of the ion (K^+) to which the membrane is permeable, and z is the charge of that ion (+1). The activity is equal to the product of the ionic activity coefficient (γ_+) and the concentration of the ion (M),

$$A = \gamma_+ \, M \qquad (4)$$

and γ_+ is a function of ionic strength and ionic interactions (such as complexation). Ideally, the electrode pair should be calibrated with standard solutions of known activity and fit to Equation (3). In a plot of E (in millivolts) versus the logarithm of the activity, the slope should be equal to the Nernst slope (2.3 RT/zF) and the intercept equal to E° if the sensor has a true Nernstian response. For practical applications, the electrode potential (E) is plotted as a function of the log of the concentration (M) to provide a working curve for concentration measurements in unknown solutions. Since the ionic activity sensed by the electrode is not equal to the true concentration due to background interferences, the electrode must be calibrated in standard solutions

which duplicate the background matrix effects of the sample. For example, an electrode measurement in seawater requires calibration of the sensor in standard seawater solutions.

Two types of potassium electrodes were evaluated in this study: two glass electrodes and a liquid ion-exchange electrode, all of which were quite different in construction and selective processes. The glass electrodes have a sensing element made of a thin-layered bulb prepared from special glass. The glass electrodes are usually made from mixtures of oxides of elements with oxidation state of 3 or greater (i.e., silicon, aluminum) and oxides of elements of oxidation state 1 or 2 (i.e., K^+, Na^+). When they are melted and subsequently cooled, these oxides form a 3-dimensional solid in which the most mobile charged-species are the monovalent cations. A membrane made of this glass is, therefore, permeable almost solely to the cation and functions as a cation exchanger. The result is that a Nernst potential is observed when such a membrane separates two solutions of a single salt at two different concentrations. The electrode is prepared by filling a thin-walled glass bulb with a solution of the salt (K^+) of constant composition. The electric potential measured using such a half cell depends only on the activity of the cation (a_i) in the external solution and, therefore,

$$E = \text{constant} + 2.3 \frac{RT}{zF} (\log a_i)$$

This provides the means to measure the activity of the cation in different solutions as long as an appropriate reference electrode is used to complete the circuit.

The liquid ion-exchange electrodes have a sensing element consisting of an organic liquid ion-exchanger dissolved in an organic solvent. The ion-exchange liquid is held in contact with the sample by means of an organophilic porous membrane surrounded by a circular porous plastic reservoir saturated with the ion-exchanger. The internal aqueous reference salt solution is on the inside of the membrane. The transport of an ion through the membrane is dependent upon the process by which the ion enters the membrane and the movement of the ion within the membrane phase. Selectivity and rejection of other ions is achieved by blocking the ability of the ion to pass through the membrane solution interface or to move across the membrane. The selected ion can move freely in the membrane by diffusion. Since the liquid phase is in contact with the aqueous sample solution, it must be water insoluble and have a low vapor pressure to prevent significant evaporation. In most cases the liquid phase is a relatively low dielectric-constant, high molecular-weight organic liquid allowing the site and the ion to move together through the membrane phase. At the membrane interface, a process of ion exchange takes place between the ions of the ion-site in the organic phase and the free ions in the aqueous phase.

The reference electrode is that half of the electrode pair which provides a constant reference potential regardless of solution composition. The potential developed by the sensing electrode is

measured against the reference potential to yield an overall system potential that is proportional to the activity of free ions.

Two types of reference electrodes were evaluated in this study: the first type was contained within the sensing electrode referred to as a "combination electrode;" the other type was an external single-junction reference electrode with the internal filling solution chosen to form a low junction-potential liquid junction with the sample solution. A sleeve-type reference electrode was used for those sensors requiring an external reference electrode. The filling solution of the sleeve-type reference electrodes contacts the sample solution by means of a narrow ring-shaped opening between an outer sleeve and the inner body of the electrode. The space between the body and sleeve widens above the tip to form a conical reservoir of filling solution. This type of electrode provides exceptionally stable junction potentials, making them especially suitable for specific ion and precision pH measurements. The junction area, due to its size and the high leak rate of the internal filling solutions, does not become easily clogged as in the case of the frit-type, or ceramic, junction reference electrodes.

Many of the problems with ion-selective electrodes can be traced to the liquid junction in the external reference electrode. The problem can be clarified if one compares the ion-selective electrode measurement with a typical pH measurement. Most laboratory pH measurements are made to an accuracy of 0.1 pH units, which corresponds to approximately 6 mV in electrode potential. However, with specific ion sensors, the analyst usually tries to obtain 1-2% in the activity of the ion being measured. This requires an accuracy of 0.1 to 0.2 mV. Any irreproducibility or drift in the liquid-junction potential becomes much more apparent in specific ion measurements. In this evaluation, we used the same reference electrode for all measurements to eliminate possible differences in electrode response due to the reference electrode. Duplicate runs were also made with another reference electrode. Both reference electrodes gave the same results for calibration curves and response times.

Significant liquid-junction potentials arise anytime two solutions of different compositions are brought into contact (i.e., internal filling solution and the sample solution). The potential results from the interdiffusion of the ions in the two solutions. Since different ions diffuse at different rates, the electrode charge will be carried unequally across the solution boundary, resulting in a potential difference between the two solutions. For reliable electrode measurements, liquid-junction potentials in the standardizing solutions must be equal to that in the sample solutions. Sensors for seawater analyses, therefore, must be calibrated in standard solutions with a background matrix similar to seawater. If this procedure is not followed, the change in liquid-junction potential between the standard solutions and the sample will appear as an error in the measured electrode potential. The structure of the reference electrode can also

cause liquid-junction problems. A small continous flow of the reference filling solution into the sample solution must be maintained. The velocity of the flow must be just enough to overcome back-diffusion of sample ions into the junction itself. Otherwise, there would be a steady buildup of sample ions inside the junction which would, in time, give rise to variations in the junction potentials. The reference electrodes used in this evaluation were constructed to eliminate the problem.

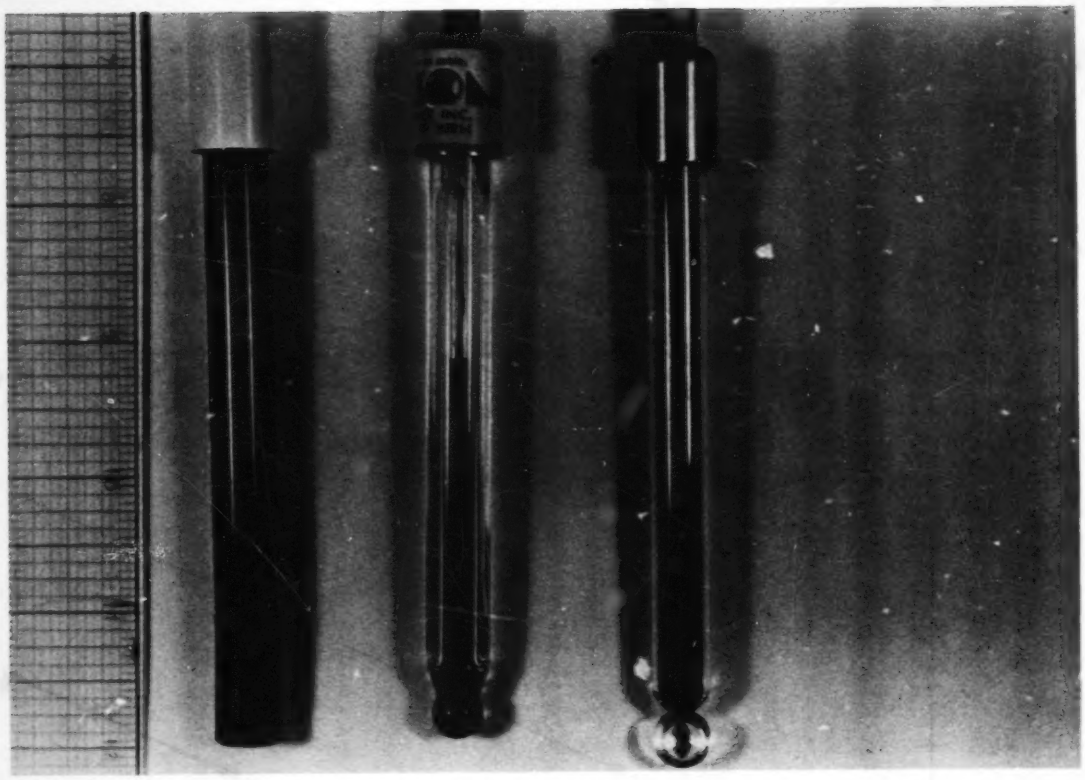

Figure 1. The Orion, Markson, and Thomas potassium electrodes.

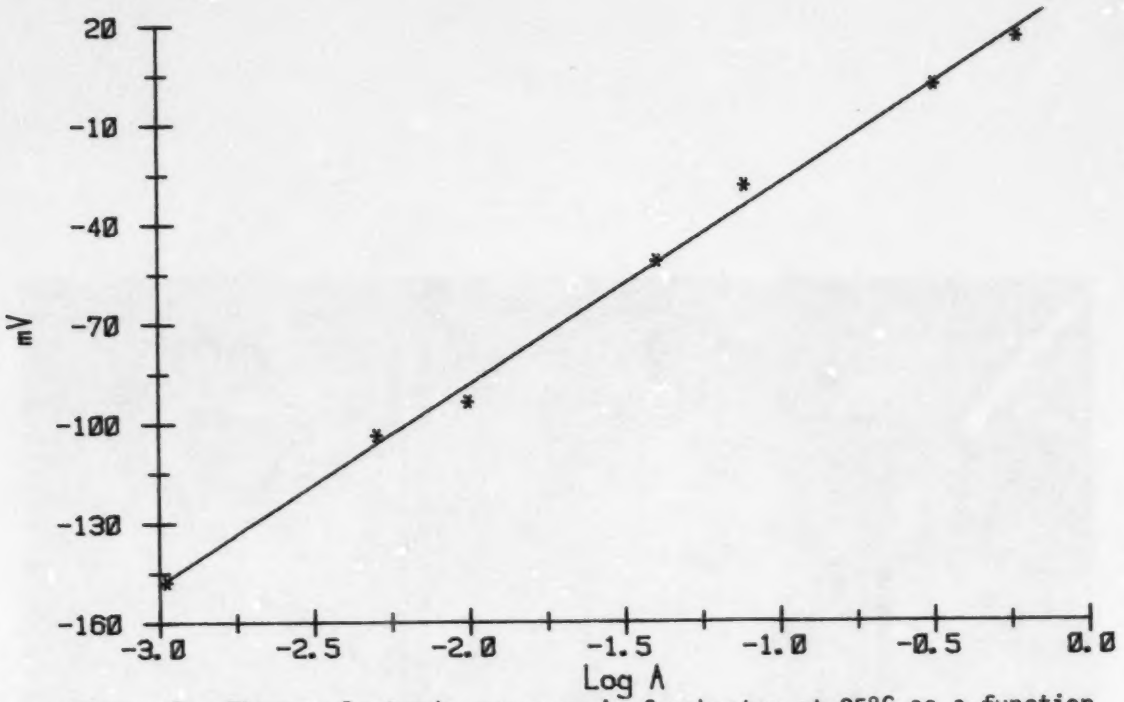

Figure 2. Thomas electrode response in freshwater at 25°C as a function of the logarithm of the potassium activity.

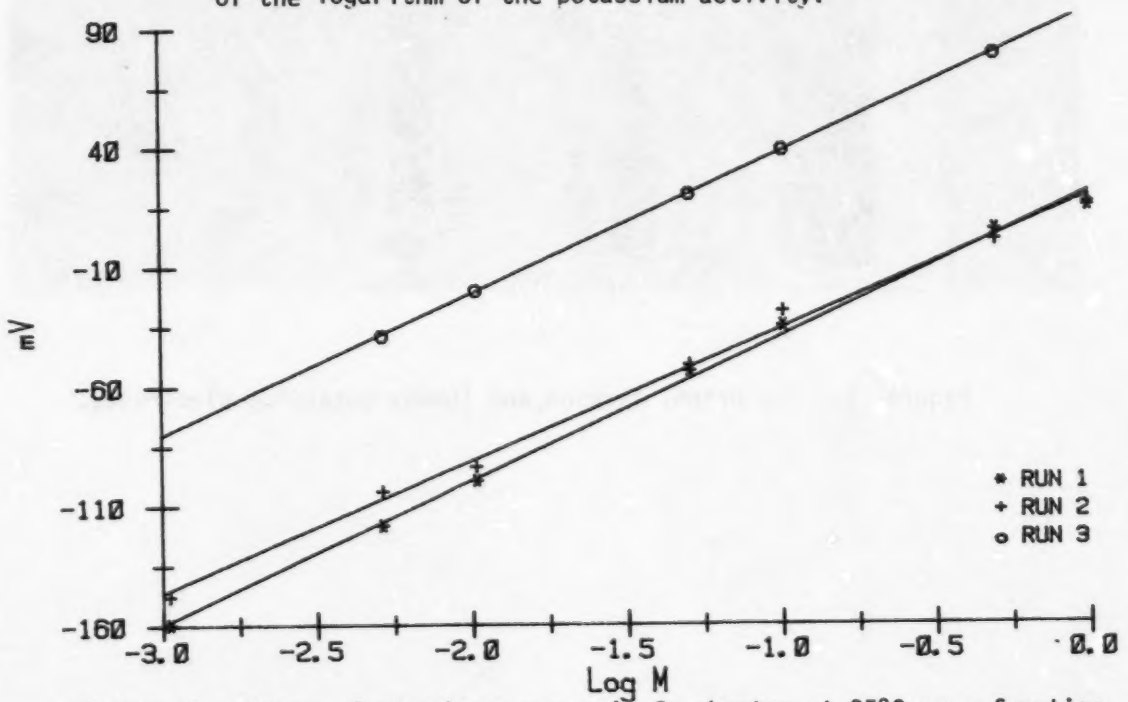

Figure 3. Thomas electrode response in freshwater at 25°C as a function of concentration.

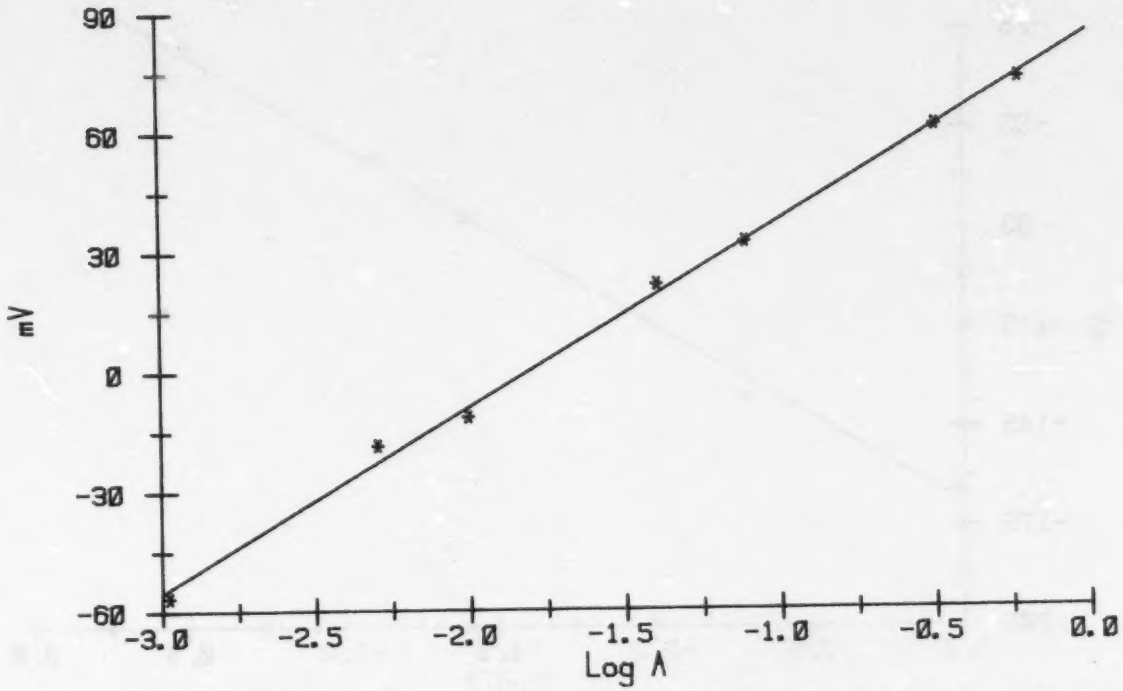

Figure 4. Markson electrode response in freshwater at 25°C as a function of the logarithm of the activity.

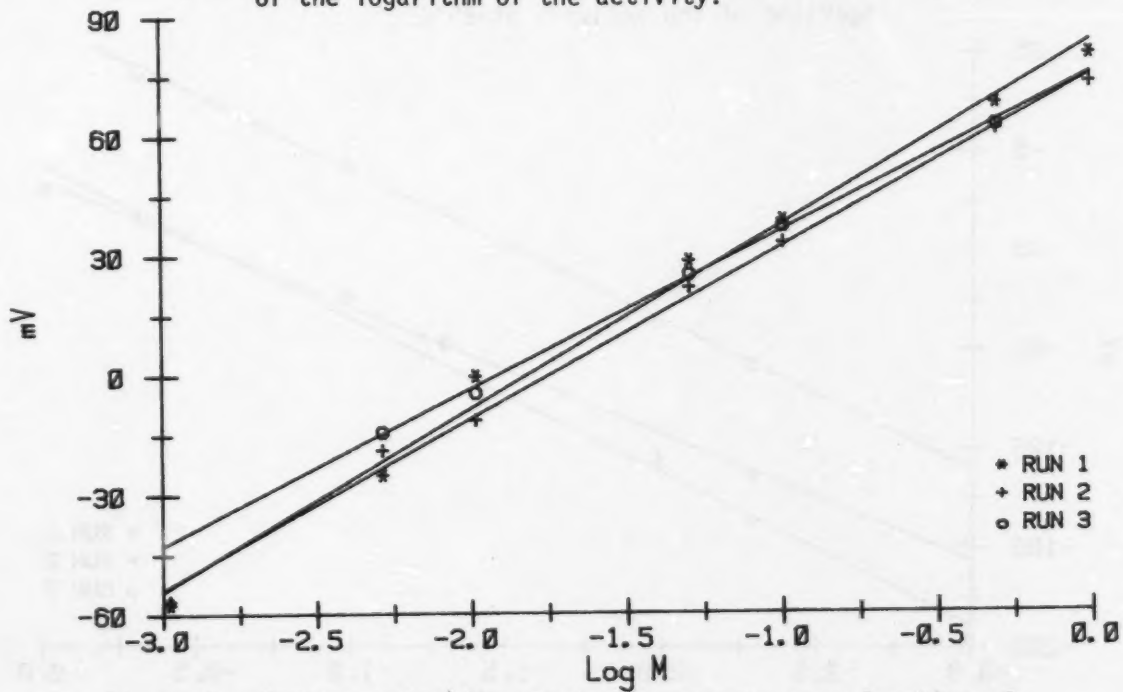

Figure 5. Markson potassium electrode response as a function of concentration at 25°C.

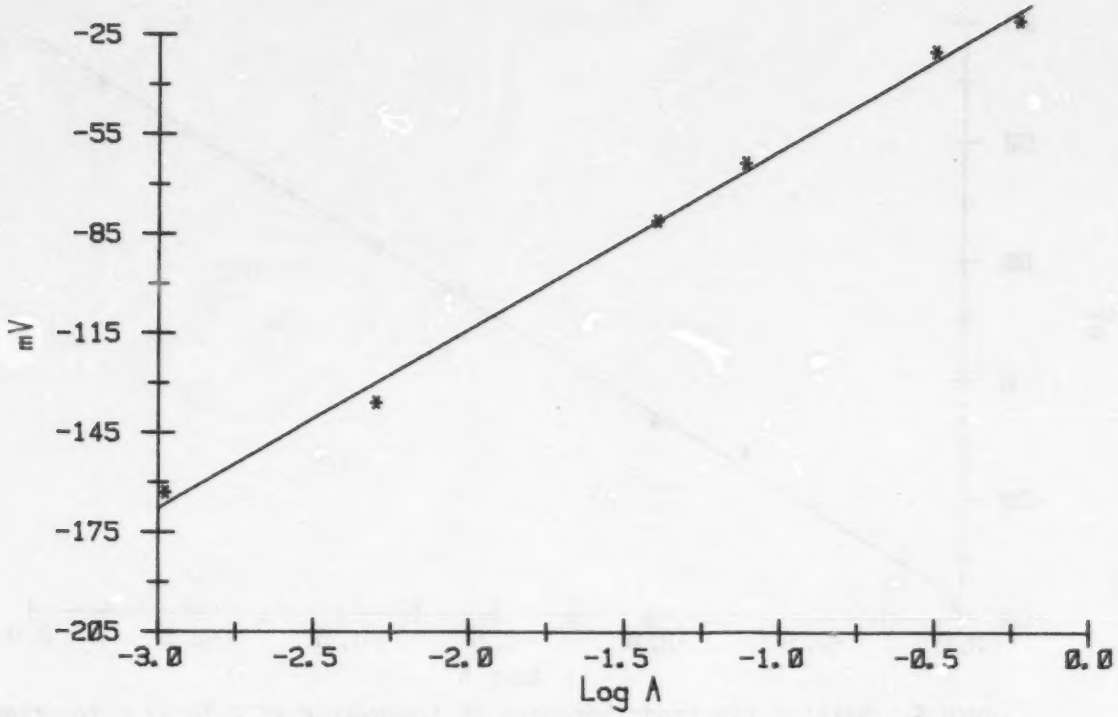

Figure 6. Orion potassium electrode response as a function of the logarithm of the activity at 25°C.

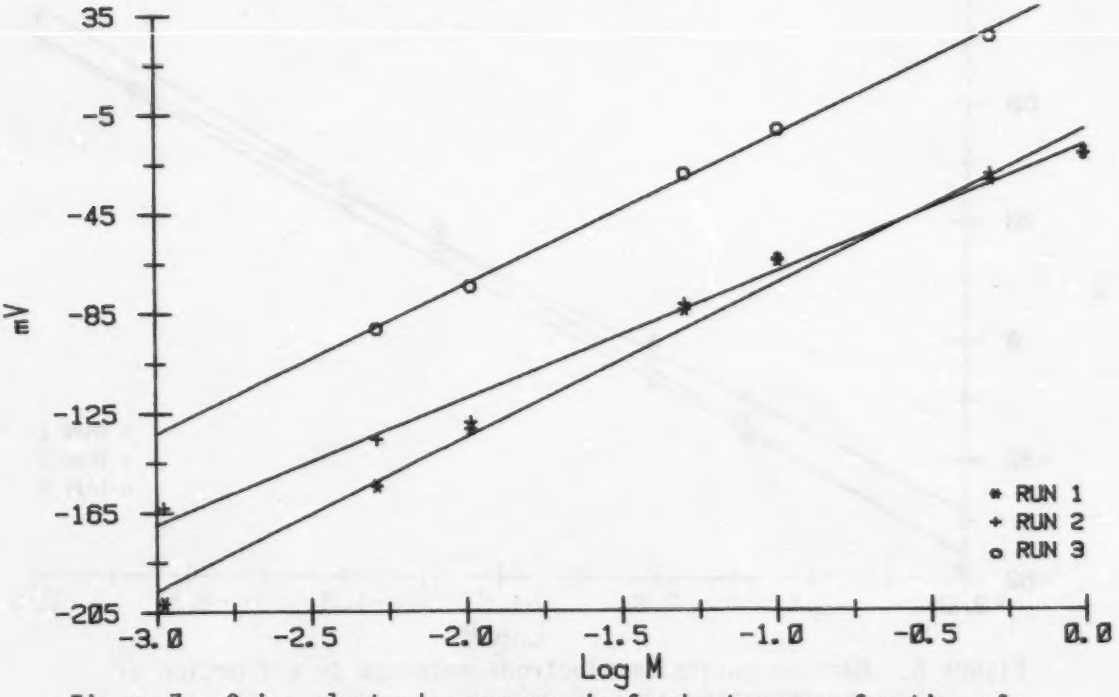

Figure 7. Orion electrode response in freshwater as a function of concentration.

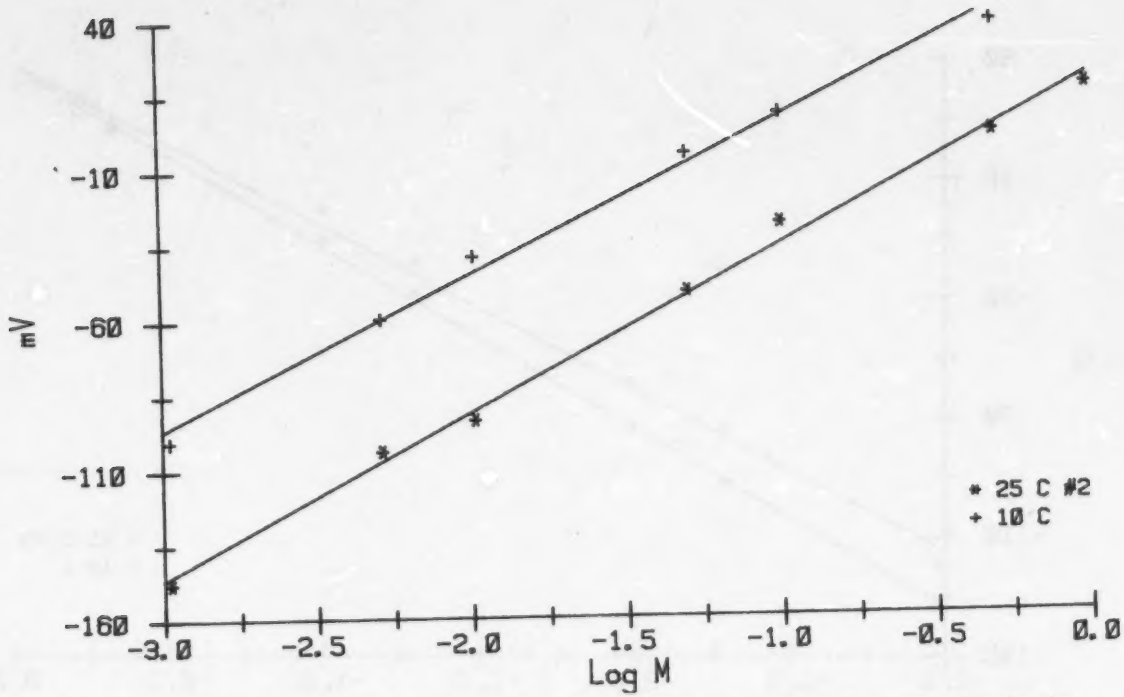

Figure 8. Temperature dependence of the Thomas potassium electrode in freshwater.

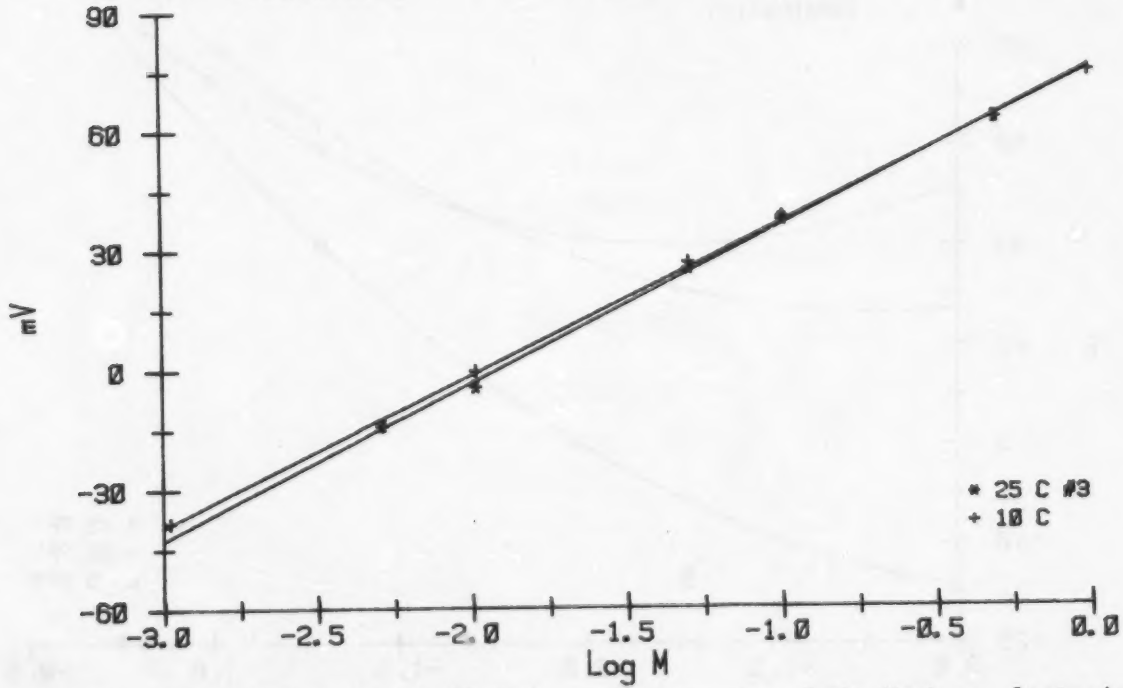

Figure 9. Effect of temperature on the response of the Markson electrode in freshwater.

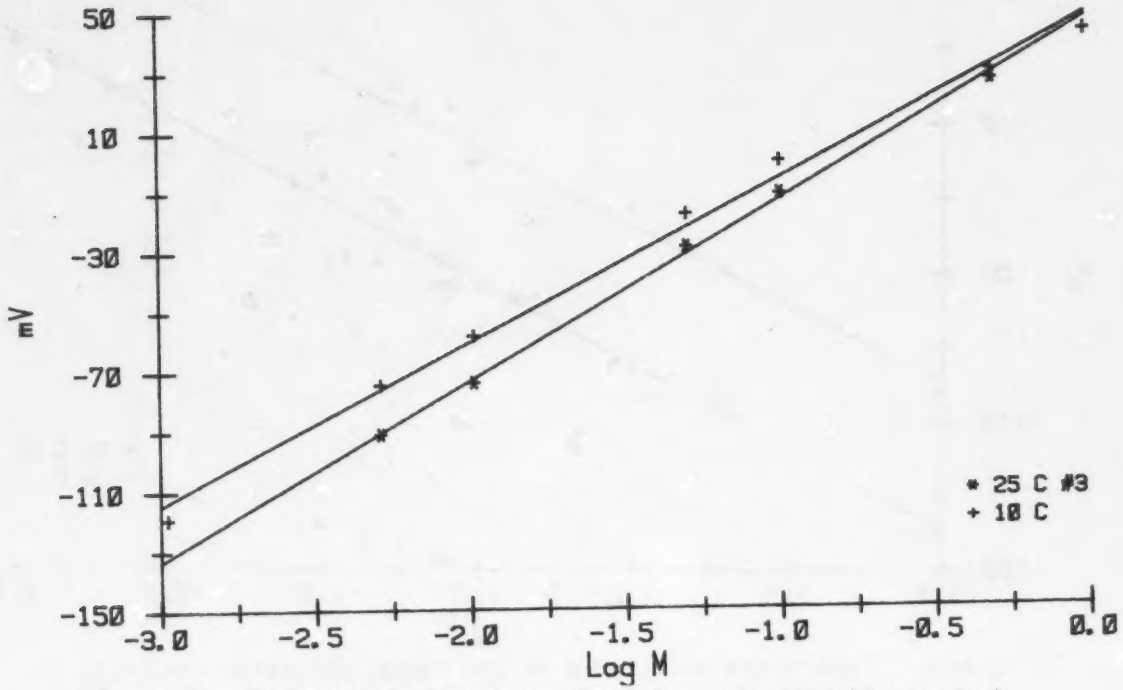

Figure 10. Temperature effect on the Orion potassium electrode in freshwater.

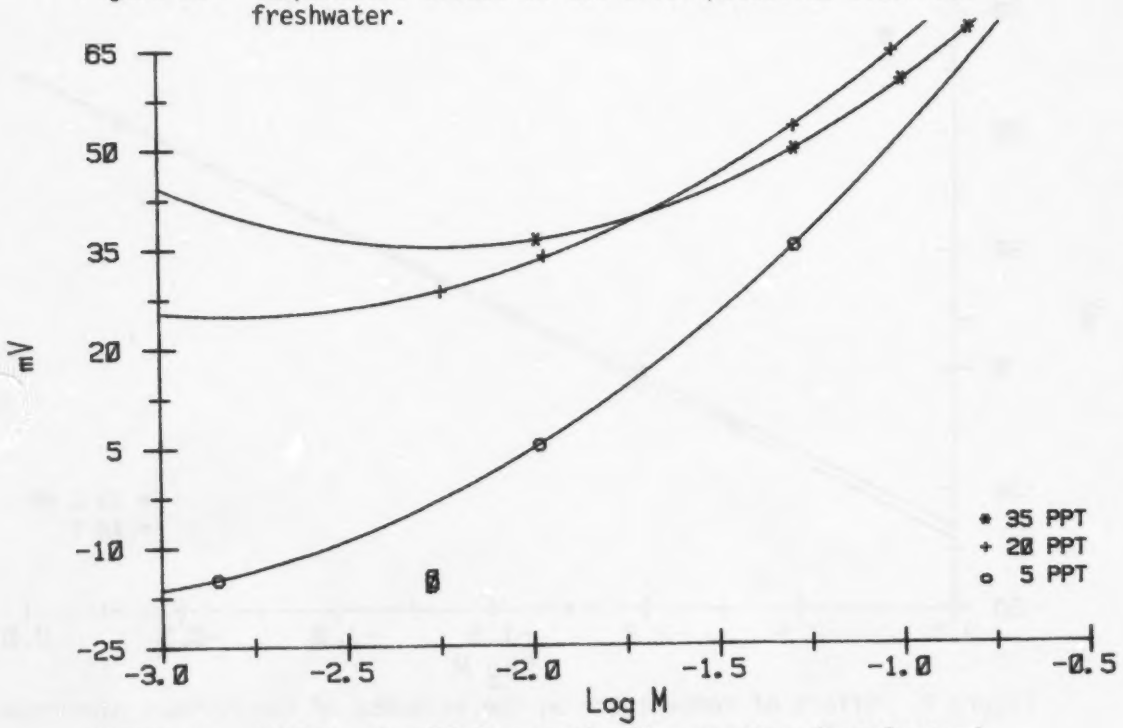

Figure 11. Effect of salinity on the Thomas potassium electrode at 25°C in seawater.

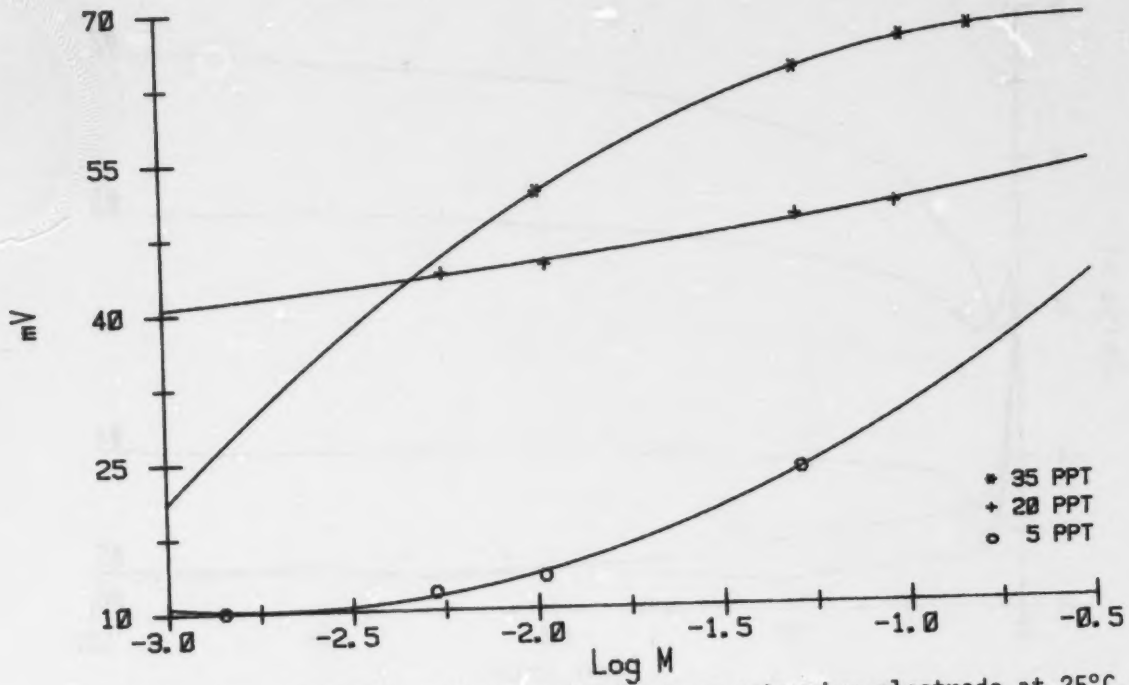

Figure 12. Salinity effects on the Markson potassium electrode at 25°C.

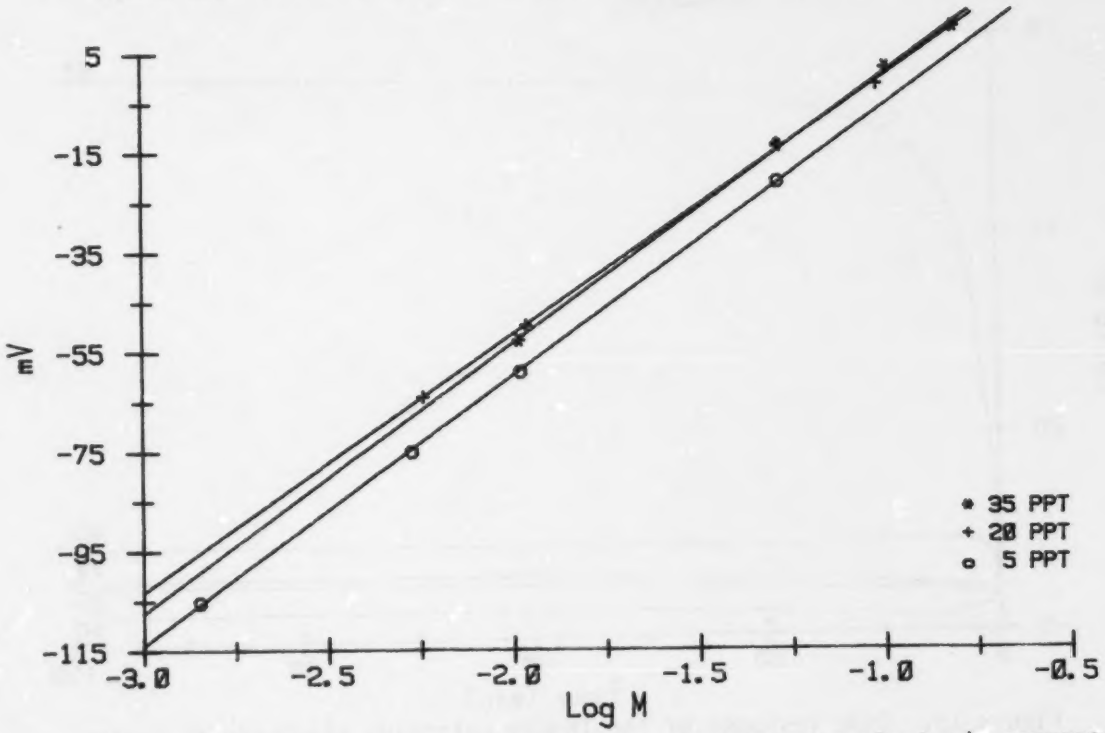

Figure 13. Effect of salinity on the Orion potassium electrode response at 25°C in seawater.

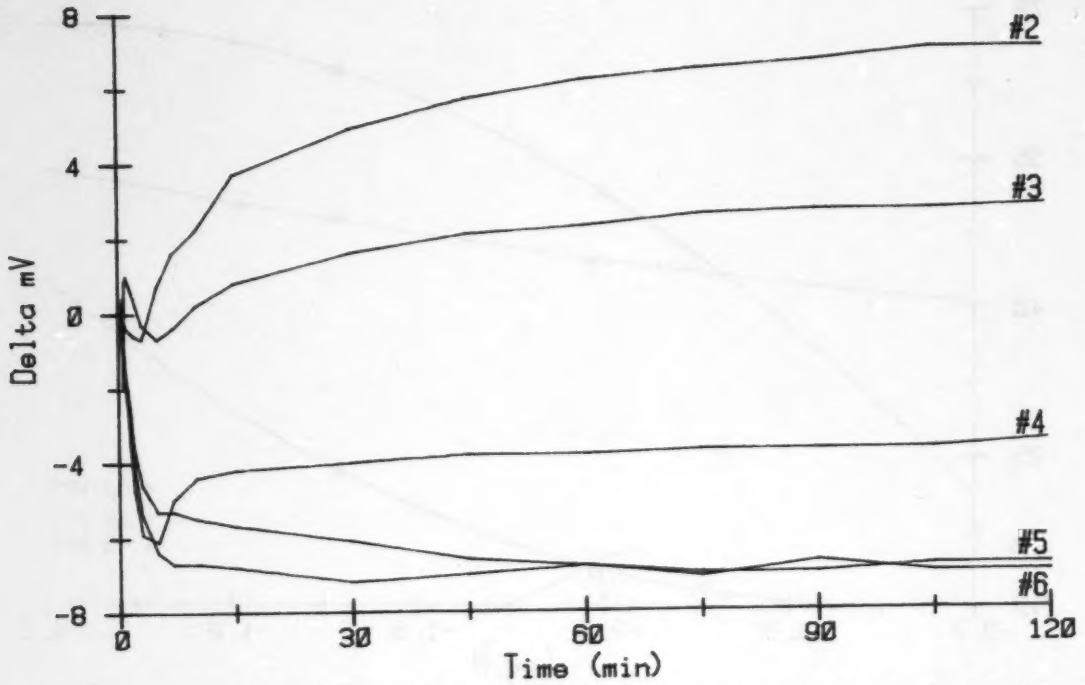

Figure 14. Time response of the Thomas potassium electrode in Run #1 at 25°C in freshwater.

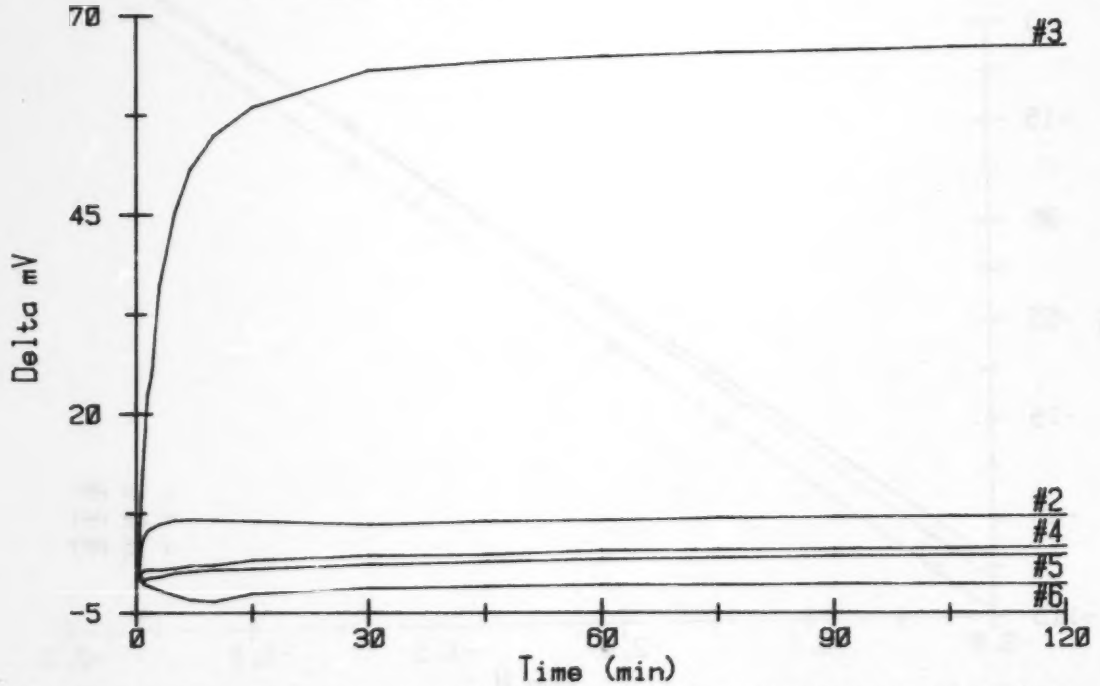

Figure 15. Time response of the Thomas potassium electrode in various concentrations of potassium in Run #3 in freshwater.

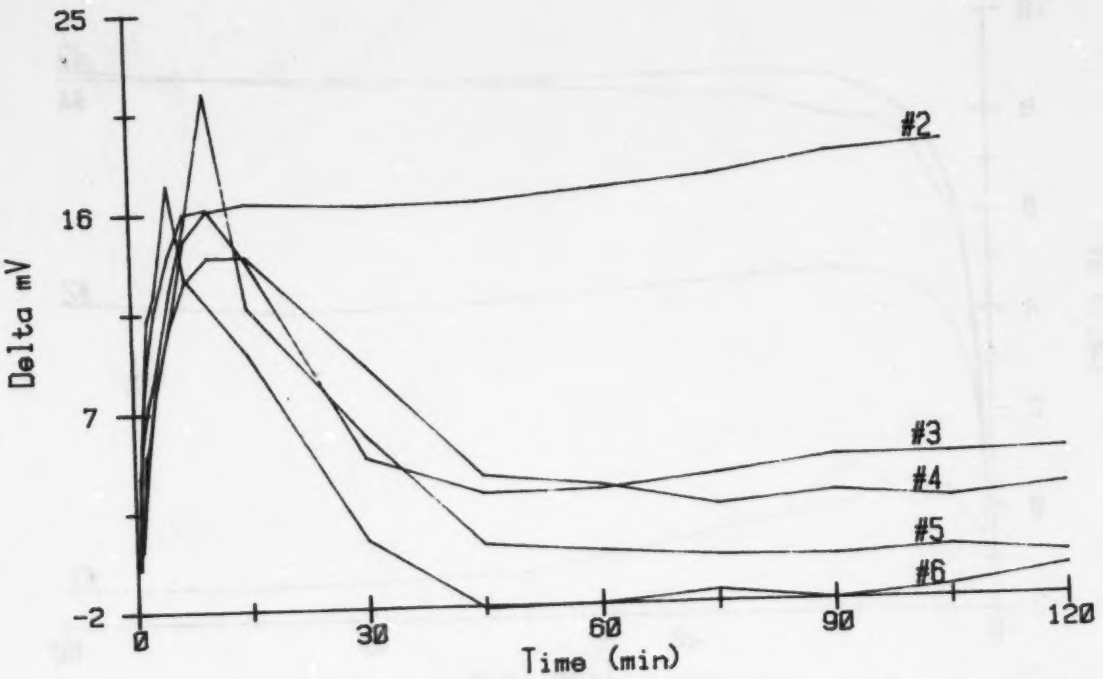

Figure 16. Time response of the Thomas electrode at 10°C in freshwater solutions.

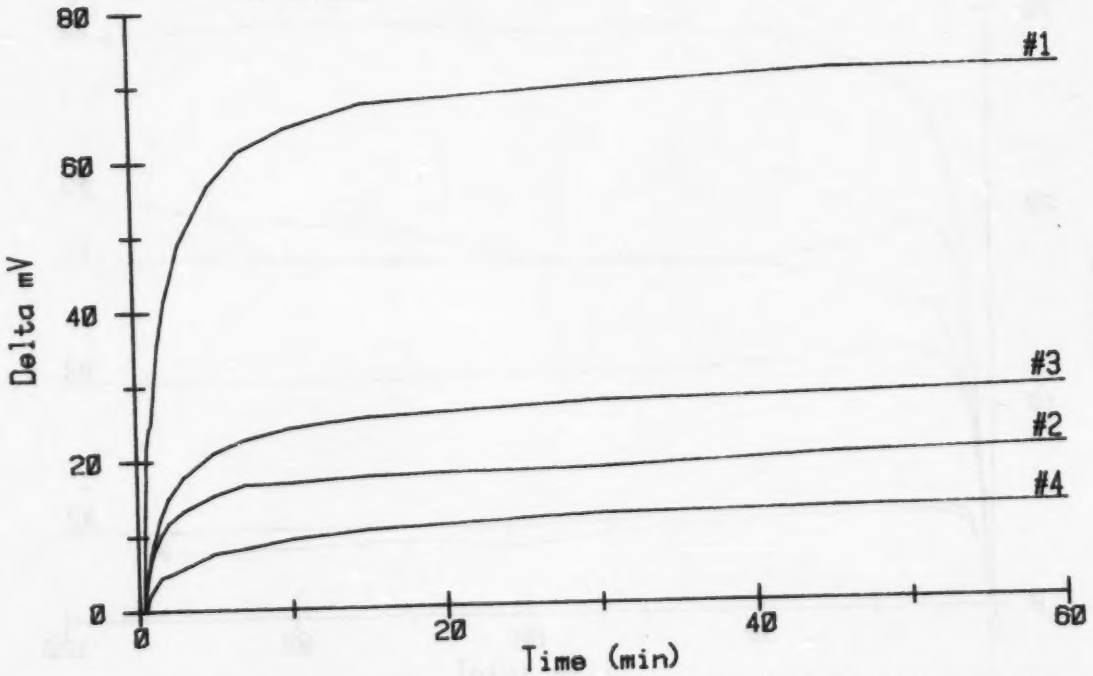

Figure 17. Time response of the Thomas electrode in 20-ppt salinity seawater.

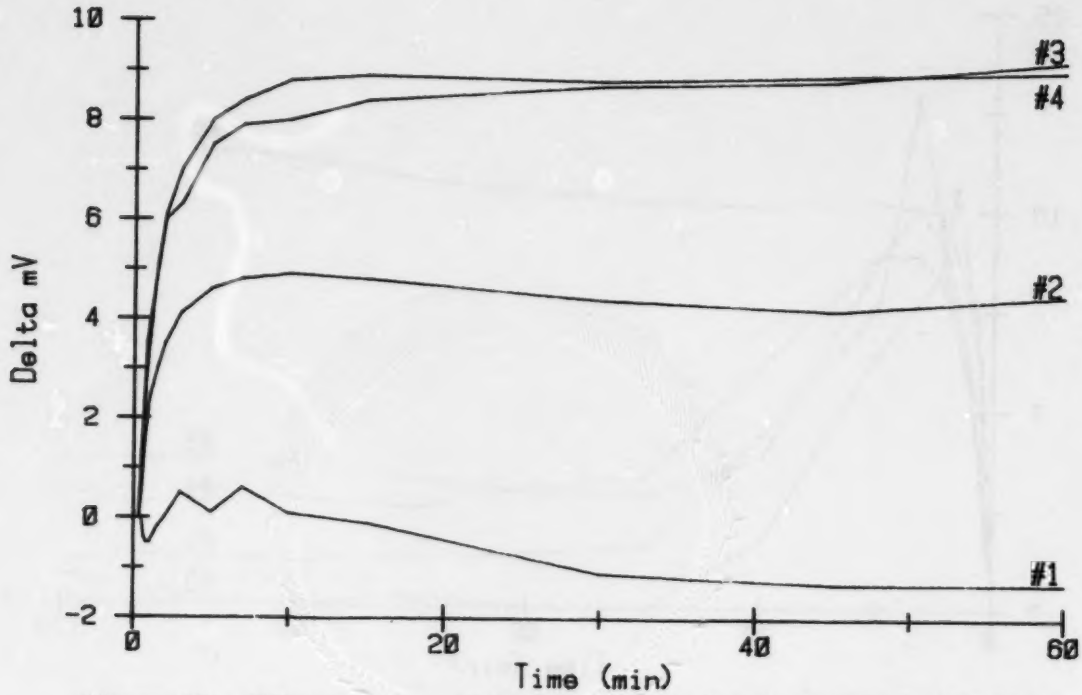

Figure 18. Time response of the Thomas electrode in 5-ppt salinity seawater at 25°C.

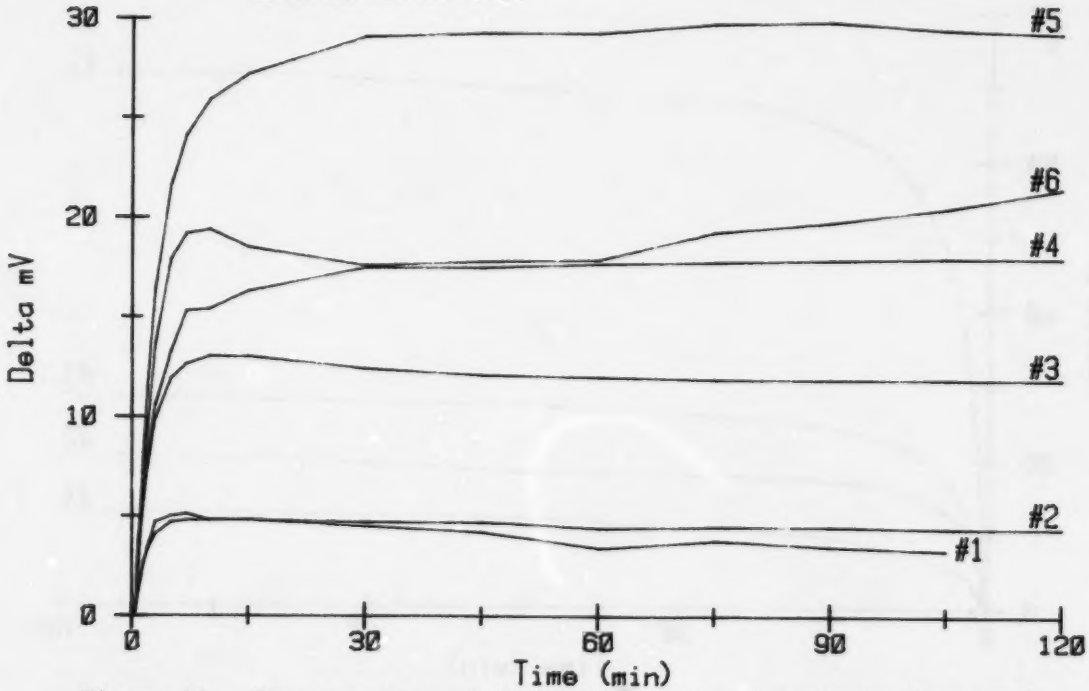

Figure 19. Time response of the Markson potassium electrode at 25°C in freshwater (Run #1).

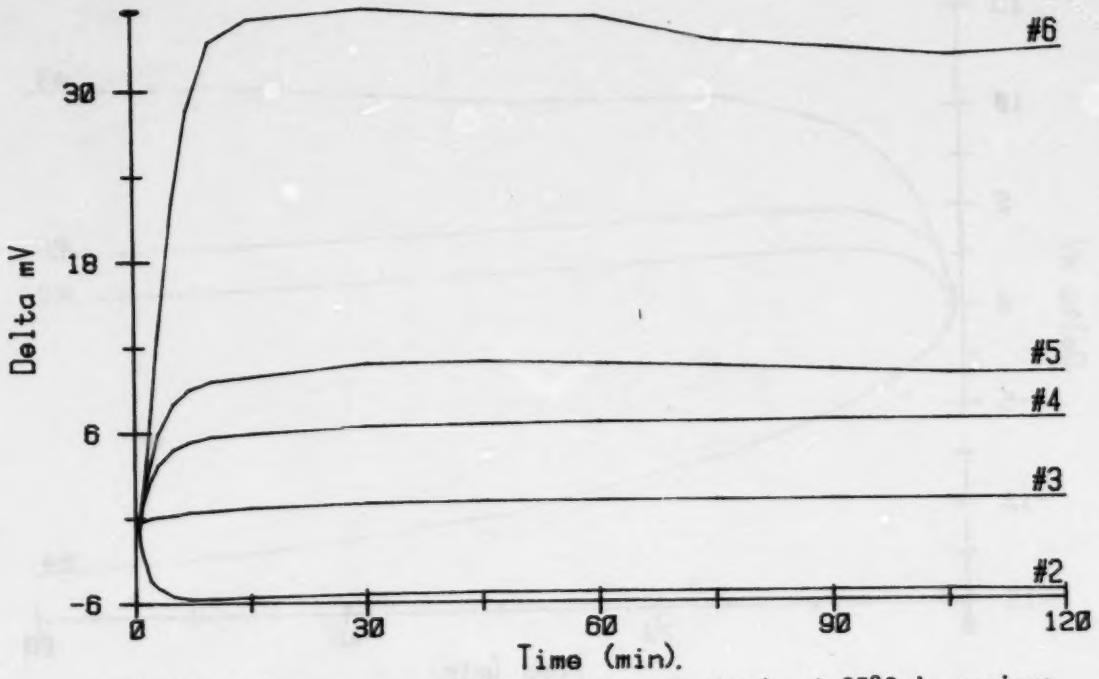

Figure 20. Time response of the Markson electrode at 25°C in various freshwater solutions (Run #3).

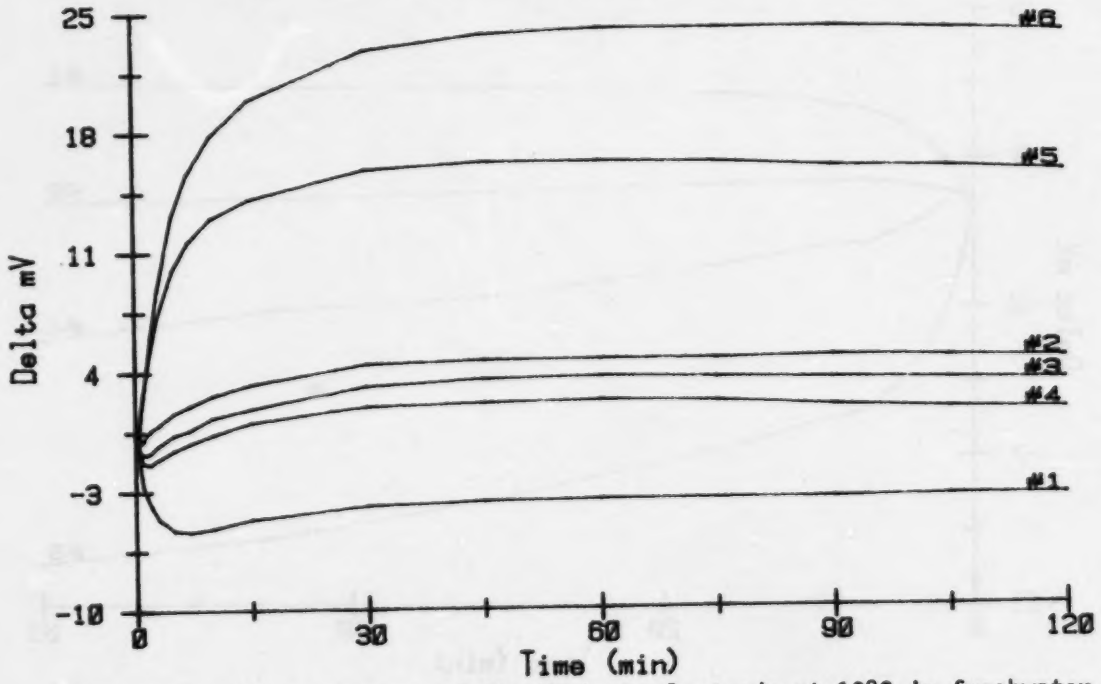

Figure 21. Time response of the Markson electrode at 10°C in freshwater solutions.

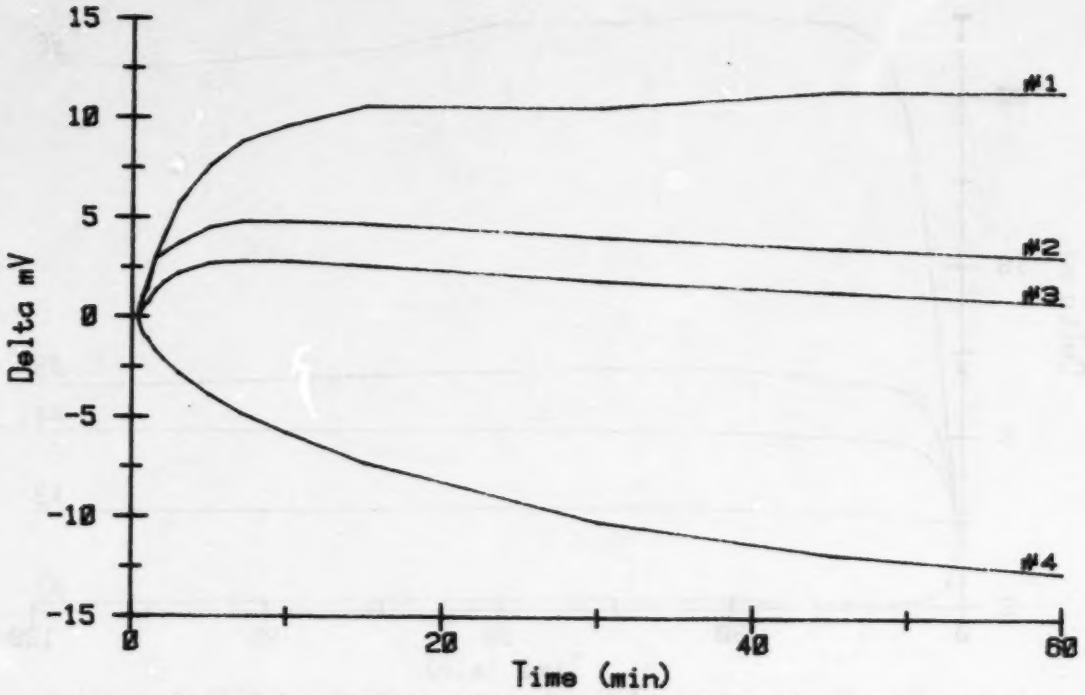

Figure 22. Markson electrode time response in 5-ppt seawater at various potassium concentrations.

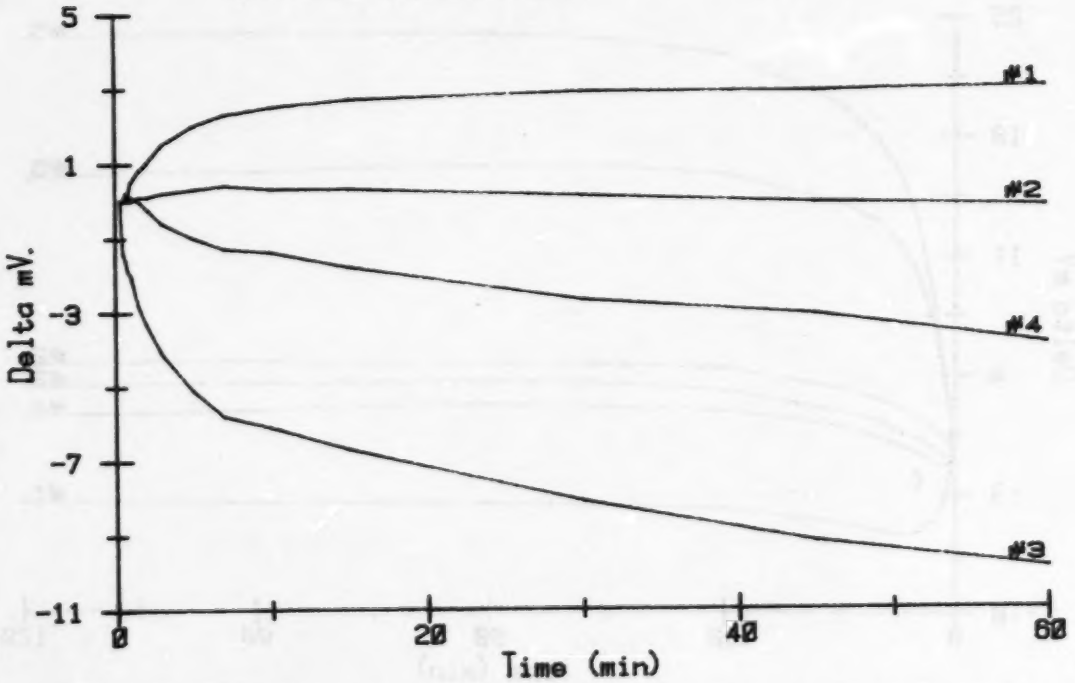

Figure 23. Time response of the Markson electrode in 20-ppt salinity seawater.

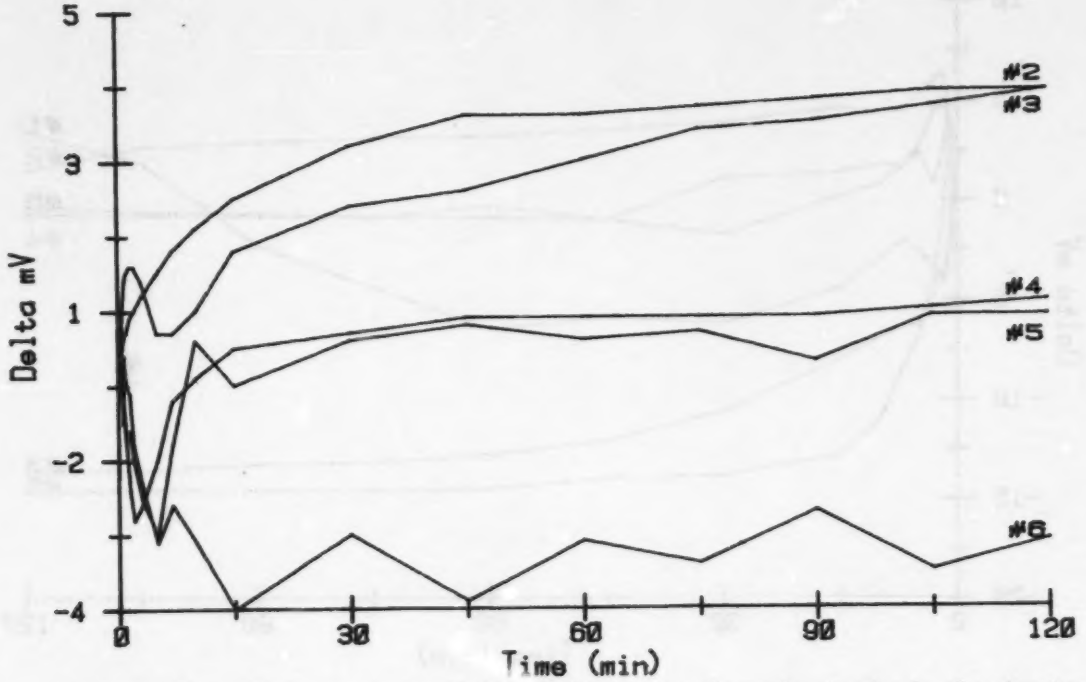

Figure 24. Time response of the Orion potassium electrode in freshwater at 25°C (Run #1).

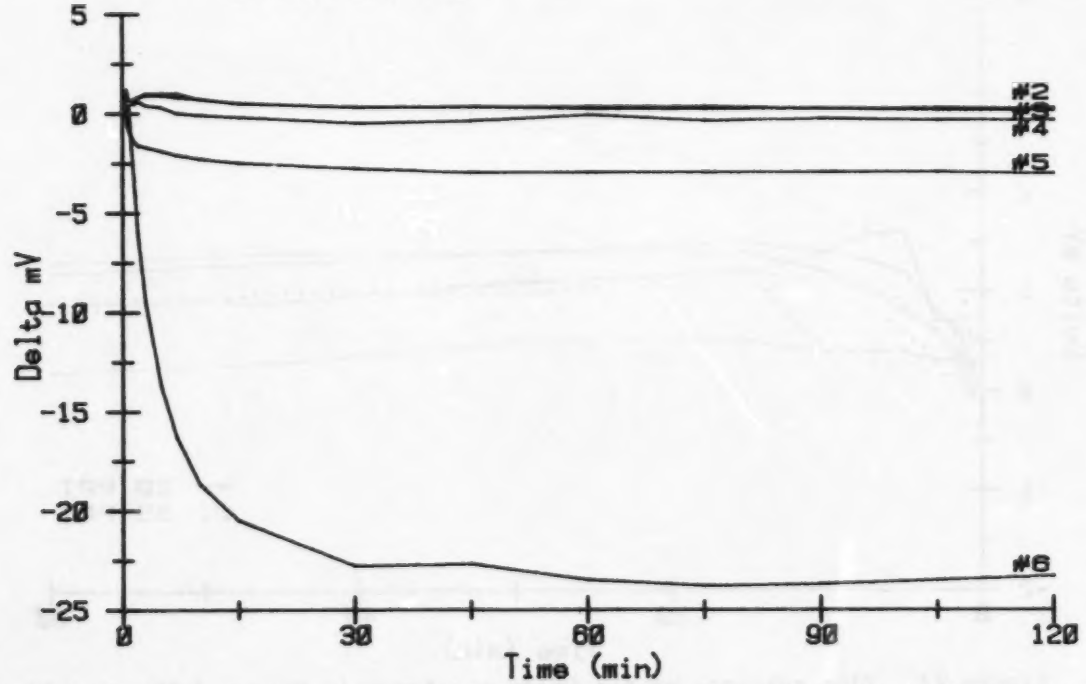

Figure 25. Time response of the Orion potassium electrode in freshwater solutions at 25°C (Run #3).

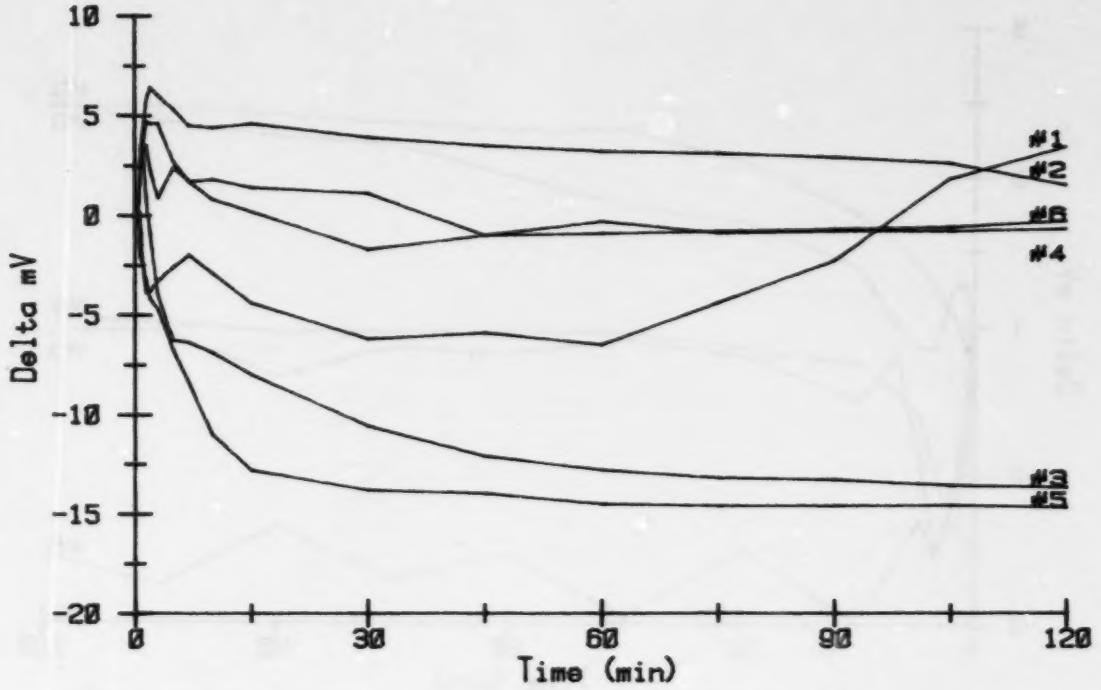

Figure 26. Orion electrode time response at 10°C in freshwater solutions.

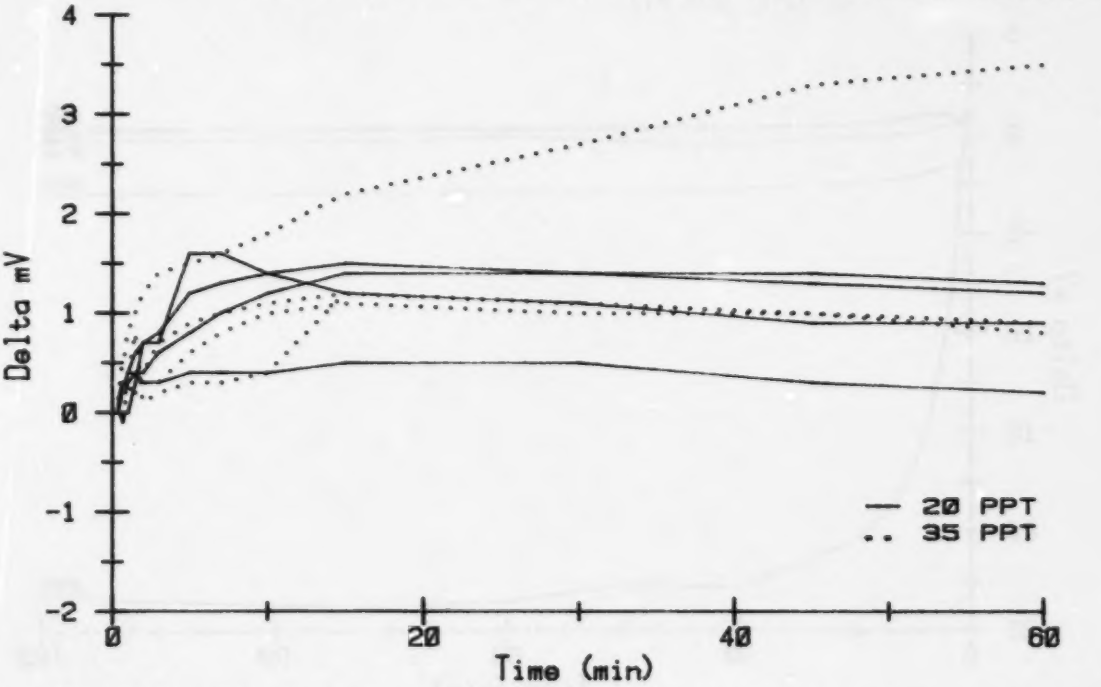

Figure 27. Time response of the Orion electrode in 20- and 35-ppt salinity seawater solutions.

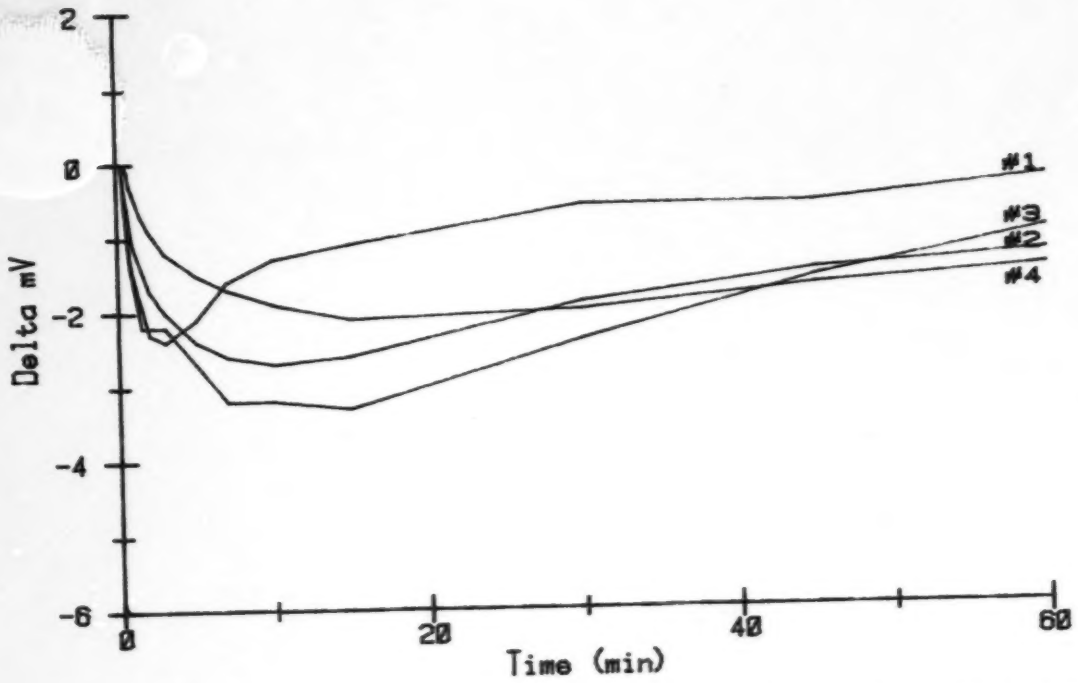

Figure 28. Orion electrode time response in 5-ppt salinity seawater for various potassium concentrations.

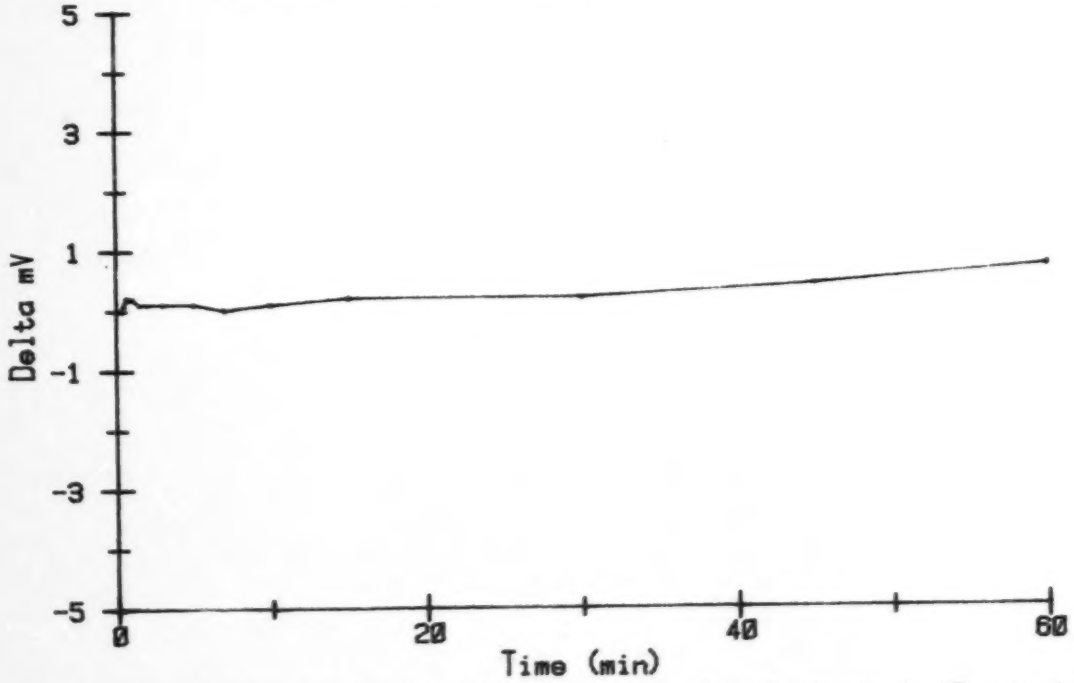

Figure 29. Time response of the Orion potassium electrode in 35-ppt standard seawater at 25°C.